Evidence for a Ring-Opening Preequilibrium in the Exchange Reactions of Diosmacyclobutanes

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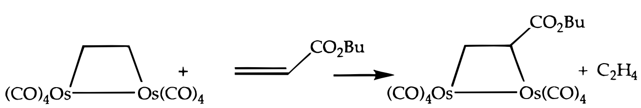
Abstract: Variable-temperature ^{13}C NMR does not show any evidence for intramolecular ethylene rotation in **1**-^{13}C. The rates of alkene dissociation for the propene (**8**) and *trans*-2-butene (**7**) adducts of $Os_2(CO)_8$ have been measured in hydrocarbon solution and compared with the rates of alkene dissociation from the corresponding $Os(CO)_4$(alkene) adducts **6** and **9**. The kinetic labilities of propene and *trans*-2-butene are reversed in the $Os_2(CO)_8$(alkene) and $Os(CO)_4$(alkene) systems; propene is replaced 2.5 times faster than *trans*-2-butene in the $Os_2(CO)_8$(alkene) system, while *trans*-2-butene is replaced 55.9 times faster than propene in the $Os(CO)_4$(alkene) system. We have used molecular mechanics to explore the reasons for this unusual reactivity pattern and have found that these results may be easily reconciled with a ring-opening mechanism for alkene replacement in the $Os_2(CO)_8$(alkene) system. We have confirmed that alkene exchange with $Os(CO)_4$(alkene) is dissociative, in agreement with precedent. The secondary deuterium kinetic isotope effect (KIE) has been measured for the replacement of C_2H_4 and C_2D_4 in $Os_2(CO)_8(\mu$-η^1,η^1-$C_2H_4)$ (**1**) and $Os_2(CO)_8(\mu$-η^1,η^1-$C_2D_4)$ (**1**-d_4); it is 1.30(1) at 39 °C. The measured KIE is consistent with a ring-opening associative mechanism for alkene exchange (mechanism II in the previous paper).

Introduction

The preceding paper[1] examined the kinetics of reaction 1. Both multivariate analysis of its rate as a function of [C_2H_4] and [butyl acrylate], and comparison of the observed saturation kinetics with those of the corresponding mononuclear reaction, implied that the mechanism involved associative exchange with the coordinated olefin of an intermediate.



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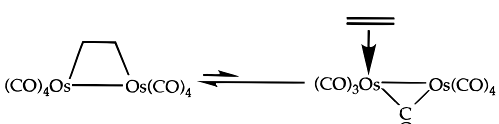
As the intermediate, we suggested **4**,[2] where the ethylene ligand that initially bridged the two osmiums of **1**, has slipped onto a single osmium (eq 2). Compound **4** has been made by

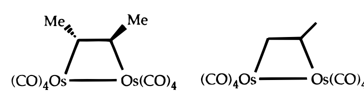


(2)

1 4

photolysis of **1** in a rare-gas matrix,[3] and observed in solution by transient IR;[4] it returns to **1** with a rate constant of 8 s^{-1} at 25 °C.[4]

We wanted evidence for an intermediate that was independent of the kinetics of reaction 1. We have therefore examined the possibility that the alkene ligand in **4** rotates,[5] leading to exchange of the ethylene carbons relative to the osmiums in **1**. Then, intrigued by the qualitative observation that the $Os_2(CO)_8$ adduct (**7**) of *trans*-2-butene appeared to be more stable than that of propene (**8**),[6] we have compared the kinetics of the exchange reactions with butyl acrylate (BA) of **7** and **8** with those of the related mononuclear complexes $Os(CO)_4$(*trans*-2-butene) (**9**) and $Os(CO)_4$(propene) (**6**); the contrast between the



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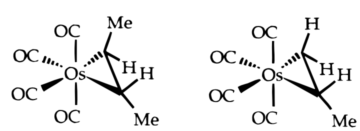

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dinuclear and mononuclear mechanisms, interpreted with the aid of *ab initio* calculations and molecular mechanics, can only be explained by the formation of an intermediate in the dinuclear case. Finally, we have examined the kinetic isotope effect for **1**/**1**-d_4 in eq 1. Secondary deuterium isotope effects have proven

⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) Ramage, D. L.; Wiser, D. C.; Norton, J. R. *J. Am. Chem. Soc.* **1997**, *119*, xxxx (preceding paper in this issue).

(2) Compounds are numbered in the same way as in the previous paper,[1] so they are not necessarily consecutive.

(3) Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497−519.

(4) Grevels, F.-W.; Klotzbücher, W. E.; Seils, F.; Schaffner, K.; Takats, J. *J. Am. Chem. Soc.* **1990**, *112*, 1995−1996.

(5) Olefin ligands in four- and six-coordinate mononuclear complexes usually rotate easily about the metal−olefin bond: (a) Alt, H.; Herberhold, M.; Kreiter, C. G.; Strack, H. *J. Organomet. Chem.* **1974**, *77*, 353. (b) Segal, J. A.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1975**, 677. (c) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (d) Mann, B. E. Non-rigidity in Organometallic Compounds. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 3, Chapter 20. The osmiums in **4** are effectively six-coordinate.

(6) Mononuclear complexes of propene are typically more stable than those of *trans*-2-butene on both electronic and steric grounds: Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163−190.

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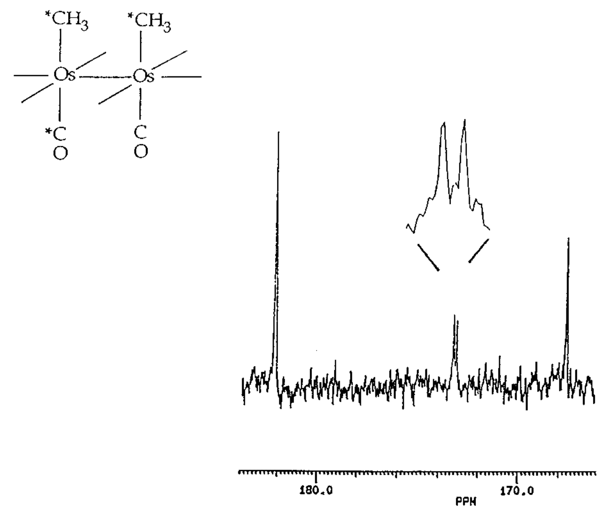
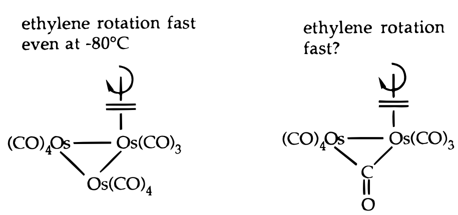


Figure 1. $^{13}C\{^1H\}$ NMR of the natural abundance carbonyl carbons trans to the methyl carbons in $Os_2(CO)_8(^{13}CH_3)_2$.

useful in distinguishing multistep mechanisms from concerted ones for pericyclic reactions (e.g., the Diels−Alder reaction).[7]

Results

Rotation of Ethylene Relative to Osmiums? While the C_2H_4 ligand is bound to a single metal in **4**, it may rotate (eq 3).[5] Such rotation has been observed for ethylene bound to a



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triosmium cluster, $Os_3(CO)_{11}(\eta^2\text{-}C_2H_4)$ (also shown in eq 3); NMR line-shape analysis has established that this rotation is fast down to −80 °C.[8] Rotation of the olefin in the intermediate **4** would (after reversal of the equilibrium in eq 2) lead to exchange of the two carbons of **1** relative to the two osmiums.

The possibility of such an exchange process can be investigated by using the $^2J(^{13}C-^{13}C)$ coupling between an sp^3 carbon of **1** and the carbonyl ligand trans to it. In $Os_2(CO)_8(^{13}CH_3)_2$ the trans carbonyl signal (δ 173.2)[9] is split by a $^2J_{CC}$ coupling constant of 11.6 Hz (Figure 1).

We prepared the diosmacyclobutane **1**-^{13}C by photolyzing $Os_3(CO)_{12}$ in the presence of $^{13}CH_2{}^{12}CH_2$. We then observed the natural abundance ^{13}C NMR spectrum of the carbonyl ligands trans to the ethylene bridge of this **1**-^{13}C.[9] In the absence of rearrangement, we expected a singlet from half of the carbonyl ligands, those opposite $^{12}CH_2$; we expected a doublet (split by $^2J_{CC}$) from the carbonyl ligands opposite $^{13}CH_2$. Exactly that spectrum was observed (Figure 2)—an apparent triplet consisted of the expected doublet, with $^2J_{CC}$ = 9.7 Hz, superimposed on the singlet.

Rotation of the ethylene relative to the two osmiums would cause this three-line pattern to collapse to a doublet with J = 4.9 Hz. The three-line pattern is observed up to 60 °C without line broadening, so there is no evidence for alkene rotation before decomposition begins. The maximum rate of alkene rotation that might be present can be estimated from the equation $k_{collapse} = \pi(\Delta \text{ line width})$. Since no line broadening was observed and the experimental line width at half-height was 0.5 Hz, the maximum line width that might have been present was 0.1 Hz, and the rate of alkene rotation must have been less than 0.3 s^{-1}.

(7) Houk, K. N.; Li, Y.; Storer, J.; Raimondi, L.; Beno, B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1599 and references therein.

(8) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (b) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

(9) We assume that the only carbonyl ^{13}C NMR signal split by the methyl or methylene ^{13}C is that of the trans carbonyl.

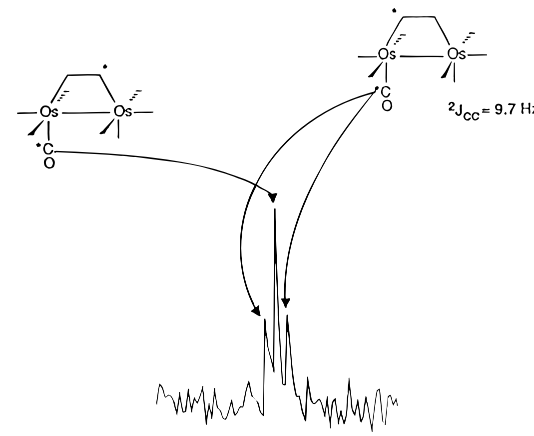
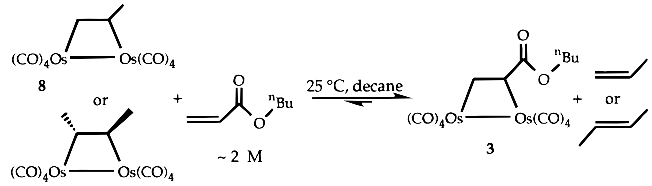


Figure 2. $^{13}C\{^1H\}$ NMR of the natural abundance carbonyl carbons trans to C_2H_4 carbons in $Os_2(CO)_8(^{13}CH_2{}^{12}CH_2)$ (**1**-^{13}C).

Table 1. Observed Rates of Reaction of $Os_2(CO)_8$ and $Os(CO)_4$ Alkene Complexes with Butyl Acrylate in Decane

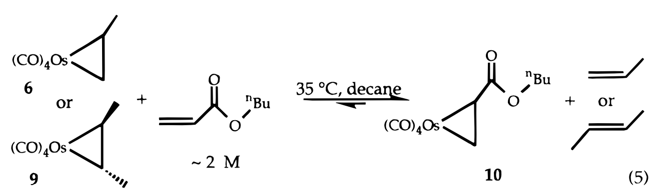
compound	T (°C)	[BA] (M)	$10^5 \times k_{obs}$ (s^{-1})
$Os_2(CO)_8$(*trans*-2-butene) (**7**)	25.0	2.017	10.11 (13)
$Os_2(CO)_8$(propene) (**8**)	25.0	1.997	24.53 (39)
$Os(CO)_4$(*trans*-2-butene) (**9**)	35.0	1.999	20.01 (47)
$Os(CO)_4$(propene) (**6**)	35.0	1.996	0.358 (10)

Kinetics of the Reactions of the Diosmium and Monoosmium Complexes of *trans*-2-Butene and Propene (7, 8, 9 and 6) with Butyl Acrylate (BA). The observed rate constants for the reactions of the dinuclear *trans*-2-butene complex **7** and the dinuclear propene complex **8** with ca. 2 M BA (eq 4) are given in Table 1. The qualitative observation that **7** was less reactive than **8** proved correct; **7** reacted almost 2.5 times *slower* than **8** under the same conditions.



(4)

Table 1 also contains the observed rate constants for the reactions of the analogous $Os(CO)_4$ complexes **6** and **9** with ca. 2 M BA (eq 5). As expected for mononuclear olefin complexes,[6] the *trans*-2-butene complex **9** reacted more rapidly with BA than did the propene complex **6**.



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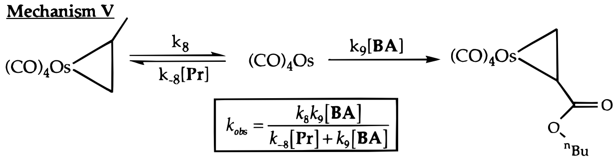
Investigation of the Mechanism of Reaction 5. In order to be able to compare the $Os(CO)_4$ olefin exchange mechanism with the $Os_2(CO)_8$ one, we have investigated the mechanism of mononuclear exchange reactions like eq 5. Huber and Poë have established a mechanism involving alkene dissociation for reaction 6,[10] and Cardaci has established a mechanism involving alkene dissociation for the reaction of $Fe(CO)_4$(alkene) with a variety of incoming ligands.[11]

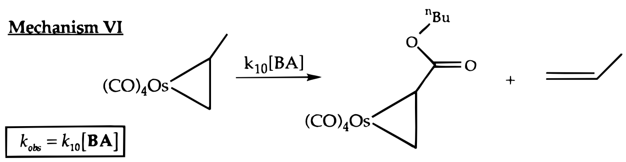
$$Os(CO)_4(\text{alkene}) + L \xrightarrow{\text{heptane}} Os(CO)_4L + Os(CO)_3L_2 + \text{free alkene} \quad (6)$$
$$L = P(OEt)_3 \text{ or } PPh_3$$

Such a mechanism has been written for $Os(CO)_4$(alkene) as mechanism V. The saturation behavior described in the preceding paper[1] ($k_8 = 3.85 \times 10^{-4}$ s^{-1} at 65 °C) is consistent with mechanism V and distinguishes it from an associative mechanism (mechanism VI).

Mechanism V

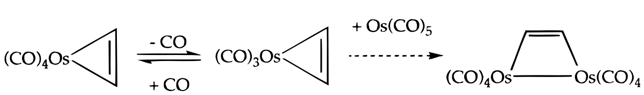


Mechanism VI



When **6** was treated with low [BA] (<1 M), the butyl acrylate complex **10** was no longer the only product. With [BA] = 0.207 M (14.2 equiv), an IR peak (2085 cm^{-1}) belonging neither to **6** nor to **10** was observed; at very low [BA] (0.0158 M, 1.09 equiv) a much larger amount of this second product appeared. Spectral subtraction (Figure A in Supporting Information) of the IR spectrum of **10** from the IR of the reaction mixture after >10 half-lives (based upon disappearance of **6**) left peaks assignable to $Os_2(CO)_8$(butyl acrylate) (**3**). No induction period was observed before the formation of **3** began.

One explanation for the formation of **3** was suggested by the reported formation of the diosmacyclobutene $Os_2(CO)_8(C_2H_2)$ from the acetylene complex $Os(CO)_4(C_2H_2)$ and $Os(CO)_5$ (eq 7).[12] The inhibition of reaction 7 by low pressures of CO revealed that reversible CO dissociation preceded addition of $Os(CO)_5$.[12]



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By analogy to the reaction between $Os(CO)_3(C_2H_2)$ and $Os(CO)_5$ one can imagine the formation of **3** from $Os(CO)_4$ and **10**, $Os(CO)_4$(butyl acrylate) (path B in Scheme 1). (Loss of CO from $Os(CO)_4(C_2H_2)$ may be preferred over acetylene loss in eq 7 because the acetylene ligand retained will be stabilized by four-electron donation, but we already know that alkene loss is preferred from $Os(CO)_4$(alkene).) One can also imagine path C, the formation of **3** by reaction of BA with the **8** generated from $Os(CO)_4$ and $Os(CO)_4$(propylene) (**6**), or even path A, the formation of **3** by reaction of BA with **2** generated from 2 equiv of $Os(CO)_4$ (**11**).

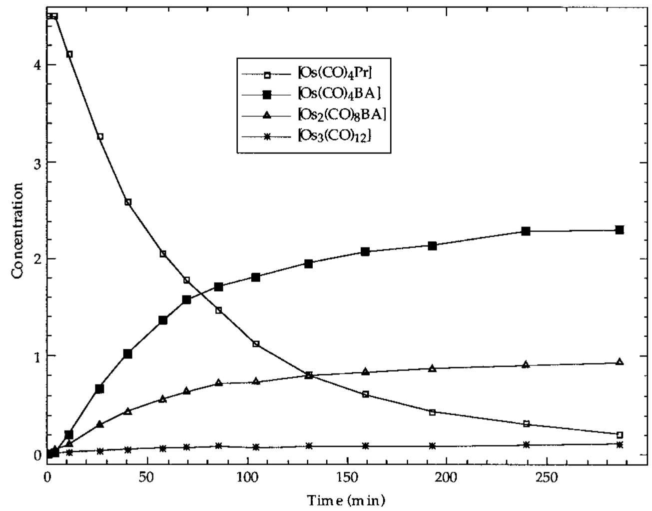
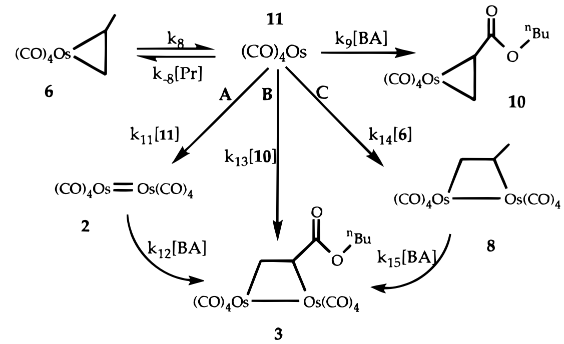


Figure 3. Concentration vs time profiles for the reaction of $Os(CO)_4$(propene) (**6**) (4.80 mM) with BA (5.46 mM) at 65 °C in decane.

Scheme 1



Path A is the least likely since the concentration of **11** is surely low. Insertion reactions like those in paths B and C have been reported previously.[12] However, path B requires an induction period for **10** to accumulate before **3** can be formed, and no such induction period has been observed in the formation of **3**. The most likely mechanism for the formation of **3** in eq 5, path C, should obey the rate law in eq 8 if k_{15} is very fast.

$$-\frac{d[\mathbf{6}]}{dt} = \frac{k_8k_9[\mathbf{6}][BA] + k_8k_{14}[\mathbf{6}]^2}{k_{-8}[PR] + k_9[BA] + k_{14}[\mathbf{6}]} \quad (8)$$

Because the formation of **3** only occurred at low [BA] it was not possible to keep BA in effectively constant large excess, and no analytical expression could be written for the integrated form of eq 8. We therefore explored the numerical integration programs GEAR/GIT, developed at du Pont.[13] For each mechanism the unknown rate constants were iteratively varied, and the concentrations of [**6**], [**10**], and [**3**] were calculated as a function of time and compared with those observed when reaction 5 was repeated with [BA]:[**6**] = 1.2 (Figure 3, and Tables B and C in Supporting Information).

A much closer fit to the experimental data was calculated with path C than with path B. (See Figures C and D in Supporting Information.) Qualitative verification that the formation of **3** in reaction 5 proceeds by path C is provided by

(10) Huber, B. J.; Poë, A. J. *Inorg. Chim. Acta* **1995**, *227*, 215–221.
(11) (a) Cardaci, G. *Int. J. Chem. Kinet.* **1973**, *5*, 805–817. (b) Cardaci, G. *J. Organomet. Chem.* **1974**, *76*, 385–391. (c) Cardaci, G. *Inorg. Chem.* **1974**, *13*, 2974–2976.
(12) (a) Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850–6852. (b) Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561–563.
(13) (a) Stabler, R. N.; Chesick, J. *Int J. Chem. Kinet.* **1978**, *10*, 461–469. (b) McKinney, R. J.; Weigert F. J. Project SERAPHIM, program number IB-1407,8. (c) Weigert, F. J. *Comput. Chem.* **1987**, *11*, 273.

Table 2. *Ab Initio* Energies for the C_2H_4 Species, Normalized with Respect to **1**

species	energy (kcal/mol)
1	0
12	30
4	14

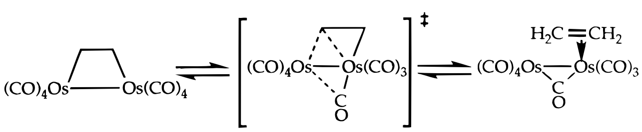
Table 3. Calculated Molecular Mechanics Energies for the Propene Species

$Os_2(CO)_8$(propene)	steric energy (kcal/mol)	δ^a (kcal/mol)	relative energy^b (kcal/mol)
starting material	21.1	0.5	0.5
transition state	22.3	−0.1	29.9
intermediate	20.7	0.6	14.6

^{a} Difference between steric energy contributions of corresponding propene and ethylene species. ^{b} *Ab initio* energies + differential steric energy.

the time dependence (Figure 3) of the concentration of $Os(CO)_4$(BA) (**10**). If path B were followed, **10** would be *both* product *and* intermediate, so a plot of its concentration vs time should rise and fall; with path C **10** is only a product, so its concentration vs time should rise monotonically—as it does in Figure 3.

Molecular Modeling of the Transition State for Ring Opening (12) and of the Ring-Opened Intermediate (4). The results above demonstrate that (a) the *dinuclear* propylene complex **8** is *more* reactive than the *trans*-2-butene one **7** in eq 4, but (b) the *mononuclear* propylene complex **6** is *less* reactive than the *trans*-2-butene one **9** in eq 5. In an effort to assess the role of steric effects in these alkene exchange reactions we have carried out a molecular mechanics study of substituted diosmacyclobutanes. The geometries of the diosmacyclobutane **1** and the slipped or "ring-opened" intermediate **4** (introduced in eq 2 above) were calculated by *ab initio* methods, as was the geometry of the transition state (**12**) between the two (eq 9);



1 **12** **4** (9)

the energies calculated for **4** and **12** relative to **1** are shown in Table 2. The relative energies of the substituted analogs of **1**, **12**, and **4** in Tables 3 and 4 were obtained by adding appropriate differential steric energies to the relative *ab initio* energies.[14−17]

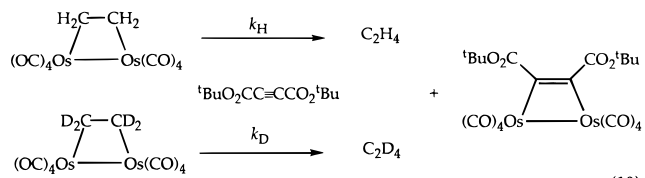
(14) The geometries of the diosmacyclobutane **1** and the slipped or "ring-opened" intermediate **4** were calculated using an RHF wave function and the basis set and effective core potential described in the Computational Details part of the Experimental Section. For **1** the calculated structure is in reasonable accord with that found experimentally by neutron diffraction.[15] The calculated Os−Os distance of 2.887 Å compares well with the neutron diffraction distance of 2.897 Å. The calculated C−C distance of 1.535 Å is in reasonable accord with the neutron diffraction distance of 1.523 Å. The calculated Os−C−C−Os dihedral angle of 11.3° is smaller than the neutron diffraction angle of 32.5°. Molecular mechanics (using the Dreiding force field[16] augmented with osmium parameters) was used to add methyl groups at appropriate positions to the *ab initio* geometries of the parent compounds (**1**, **12**, and **4**). The osmium carbonyl framework and the alkene carbon atoms were constrained to their *ab initio*-calculated positions, but the atoms of the alkene substituents were allowed to move.[17] Differential steric energy contributions, expressed as "δ" in Tables 3 and 4, were obtained by subtracting the molecular mechanics energies of the ethylene analogs from those of the substituted species. δ values are a measure of steric interactions relative to the ethylene case. The relative energies in Tables 3 and 4 were obtained by adding the δ values to the *ab initio* energies of **1**, **12**, and **4**.

Table 4. Calculated Molecular Mechanics Energies for the *trans*-2-Butene Species

$Os_2(CO)_8$(*trans*-2-butene)	steric energy (kcal/mol)	δ^a (kcal/mol)	relative energy^b (kcal/mol)
starting material	22.9	2.3	2.3
transition state	22.0	−0.4	29.6
intermediate	25.2	5.1	19.1

^{a} Difference between steric energy contributions of corresponding *trans*-2-butene and ethylene species. ^{b} *Ab initio* energies + differential steric energy.

Secondary Kinetic Isotope Effect on the Exchange of the Ethylene of 1. In order to avoid the discrepancy in temperature inevitable between independent rate measurements, the relative rates of ethylene loss from **1** and **1**-d_4 were measured by an intermolecular competition experiment at 39 °C. A large excess (0.5 M) of di-*tert*-butyl acetylenedicarboxylate (DTBAD) was used as a trap, leading to eq 10. The C_2H_4 and C_2D_4 that formed were swept away by a flow of helium and collected for analysis.



(10)

All isotope ratios were measured by GC/MS, and the kinetic isotope effect k_H/k_D calculated from the equations (based on a more general treatment for intermolecular competition) of Melander and Saunders.[18] First the KIE was determined from the initial **1**/**1**-d_4 ratio, the ratio of unreacted **1**/**1**-d_4 remaining in solution at any given time, and the extent of reaction at that time. The KIE was then determined independently by comparing the ratio of ethylenes *collected* to the initial **1**/**1**-d_4 ratio. The KIE determined from unreacted **1**/**1**-d_4 was 1.29; the KIE determined from the ratio of product ethylenes was 1.30. The average KIE for eq 10 at 39 °C, with 0.5 M di-*tert*-butylacetylene dicarboxylate as trap, can thus be given as 1.30(1).

Discussion

Alkene Dissociation from $Os(CO)_4$(alkene) and $Os_2(CO)_8$(alkene). The GEAR/GIT simulations establish that the dinuclear $Os_2(CO)_8$(BA) (**3**) formed from $Os(CO)_4$(propene) in eq 5 at low [BA] arises from path C in Scheme 1. The operation of path C is consistent with Poë's proposal (eqs 11 and 12) that $Os_2(CO)_8$(alkene) is an intermediate in eq 6. The fact that $Os(CO)_3L_2$ and $Os(CO)_4L$ are formed *simultaneously* and not *consecutively* in eq 6 (i.e., that the $Os(CO)_3L_2$ is *not* formed from the $Os(CO)_4L$) is easily explained if they are both formed from $Os_2(CO)_8$(propene).[10]

The fact that the operation of Path C and the k_9[BA] step can simulate the disappearance of $Os(CO)_4$(propene) (**6**) in Figure 3 confirms our earlier conclusion[1] that the reaction of **6** with butyl acrylate occurs by a dissociative mechanism, Mechanism V. The exchange reactions of $Os(CO)_4$(alkene) thus involve $Os(CO)_4$ (**11**) as the key intermediate.

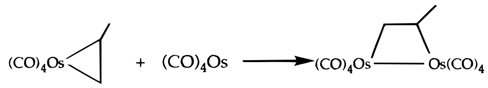
Electron-donating substituents on the alkene in $Os(CO)_4$(alkene) should decrease the ability of the alkene π^* orbital to serve as a π acceptor, repel the other ligands, and facilitate

(15) Anderson, O. P.; Bender, B. R.; Norton, J. R.; Larson, A. C.; Vergamini, P. J. *Organometallics* **1991**, *10*, 3145.

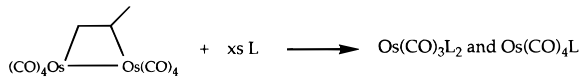
(16) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.

(17) For examples of this method, see: Eksterowicz, J. E.; Houk, K. N. *Chem. Rev.* **1993**, *93*, 2461.

(18) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; John Wiley & Sons: New York, 1980; pp 92−102.



6 11 8 (11)



8 (12)

alkene dissociation. For both electronic and steric reasons, then, we expect the lability of $Os(CO)_4$(alkene) to increase in the order $Os(CO)_4$(ethylene) < $Os(CO)_4$(propene) (**6**) < $Os(CO)_4$(*trans*-2-butene) (**9**), and this is the order we have observed.

If the alkenes in $Os_2(CO)_8$(alkene) exchanged with free olefins and acetylenes by a simple dissociative mechanism (a [$_\pi 2_s + {}_\pi 2_s$] cycloreversion), we would expect the same order of reactivity: $Os_2(CO)_8$(ethylene) (**1**) < $Os_2(CO)_8$(propene) (**8**) < $Os_2(CO)_8$(*trans*-2-butene) (**7**). The steric and electronic effects of substituents on the ease of alkene dissociation from the dinuclear $Os_2(CO)_8$(alkene) should parallel those on the ease of alkene dissociation from the mononuclear $Os(CO)_4$(alkene). (Back-bonding into the alkene π^* orbital is important in the dinuclear system also.[19]) Why then is the observed order of reactivity **1** < **7** < **8**?

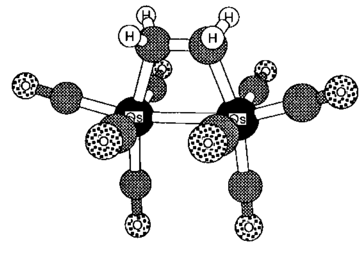
Theoretical Analysis of Possible Transition States. The ground state (**1**) and transition state (**15**) geometries calculated by *ab initio* methods for a [$_\pi 2_s + {}_\pi 2_s$] cycloreversion are shown in Figure 4. Notable changes in geometry that must occur when **1** → **15** include (1) a lengthening of the Os−C bonds as the C_2H_4 ligand moves away from the two osmiums (from 2.81 Å to 2.98 Å), (2) a flattening of the C_2H_4 ligand as the C atoms rehybidize from approximately sp^3 to nearly sp^2,[20] (3) an increase in the distance from each ethylene hydrogen to the nearest carbonyl carbon (from 2.69 Å to 2.83 Å), (4) a shortening of the ethylene C−C bond from 1.54 Å to 1.35 Å. The introduction of substituents larger than hydrogen should raise the energy of **15** less than that of **1** and should thus decrease the barrier for a [$_\pi 2_s + {}_\pi 2_s$] cycloreversion. There is no reason to expect a departure from the reactivity order **1** < **8** < **7**.

Substituents should have little effect if the *rate-determining step* is the alkene slippage ("ring opening") pictured for ethylene in eq 2. Figure 5 shows the geometry (**12**) calculated by the same *ab initio* methods for the ethylene slippage transition state; the geometry calculated for the ethylene ground state **1** is repeated for comparison. Important structural parameters for **1** and **12**, respectively, are listed in Tables E and F (Supporting Information).

The effect of alkene substituents on the transition state **12** can be assessed from the steric energy contributions calculated by molecular mechanics. Because the osmium carbonyl framework and the positions of the alkene carbon atoms were not refined during these calculations, the absolute values of the structural parameters in Tables E and F are not as reliable as their relative values—the changes that occur during alkene slippage (ring opening). An examination of these changes (listed in Table G in Supporting Information) shows some *relief* of unfavorable steric interactions in the ring opening transition state. The steric energy calculations ("δ" in Tables 3 and 4) suggest that one (the propene case) or two (the *trans*-2-butene case) methyl substituents may slightly *decrease* the barrier to ring opening.

(19) Bender, B. R.; Bertoncello, R.; Burke, M. R.; Casarin, M.; Granozzi, G.; Norton, J. R.; Takats, J. *Organometallics* **1989**, *8*, 1777.

(20) In free C_2H_4 the sum of the bond angles around each carbon is 360°. If rehybridized to sp^3 the sum of the same angles would be ≈328.5°, the sum of the three H−C−H angles in CH_4.



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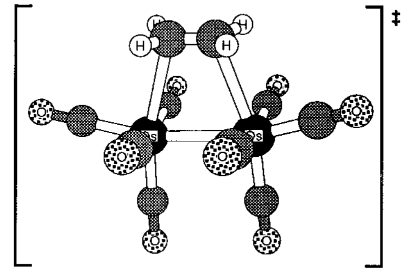
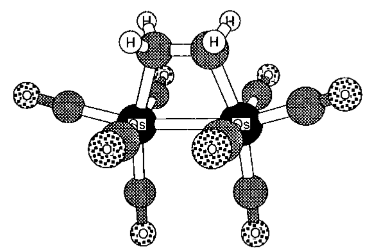


15

Figure 4. Geometries of the ground state (**1**) and of the transition state (**15**) for a concerted elimination as calculated by *ab initio* methods.



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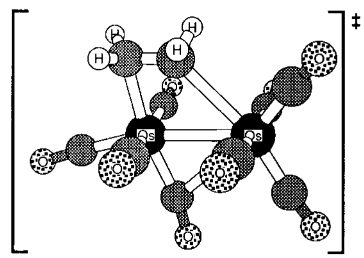


12

Figure 5. Comparison of the geometries of the ground state of compound **1** and that calculated for the transition state for ring opening, **12**.

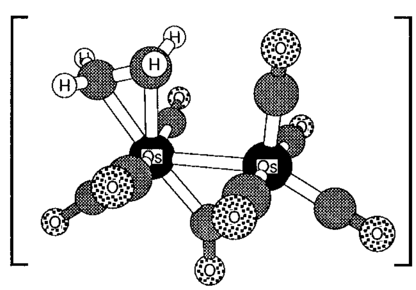


Figure 6. Structure of the ring-opened intermediate **4** as determined by *ab initio* methods.

Theoretical Analysis of the Ring-Opened 4 as an Intermediate. We now turn to the ring-opened intermediate **4**. Figure 6 shows the structure calculated for **4** by *ab initio* methods. The atom labeling scheme is shown in Figure J in Supporting Information; Table H lists the important structural parameters

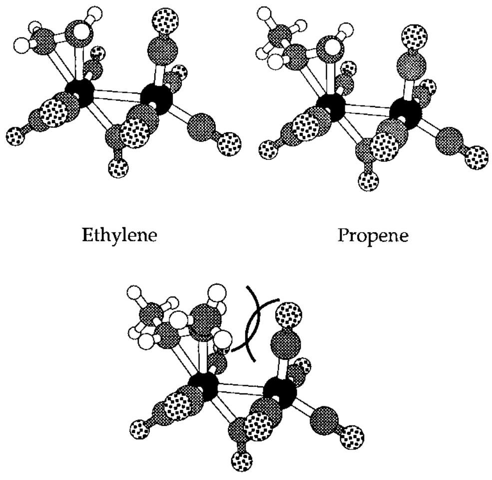


Figure 7. Comparison of the geometries of the ring-opened intermediates.

of the three differently-substituted ring-opened intermediates. The molecular mechanics calculations in Tables 2−4 (compare the "δ" values for intermediate vs starting material in Table 4 with the corresponding values in Tables 2 and 3) indicate that *two methyl substituents destabilize the ring-opened intermediate **4** by ca. 3 kcal/mol* relative to the reactant, whereas the effect of a single methyl substituent is negligible.

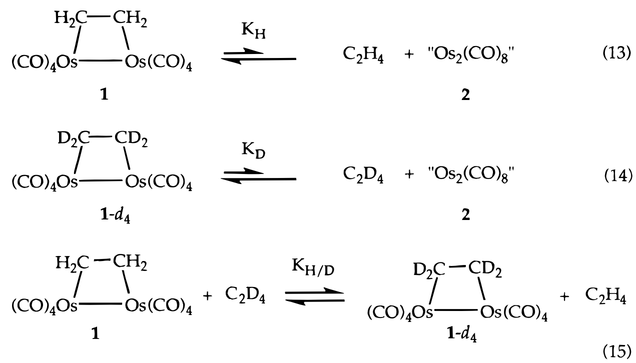
Comparison of these structures (Figure 7) suggests that the source of the destabilization is an unfavorable steric interaction between the second methyl group and a carbonyl ligand. Such an unfavorable interaction is present in neither the ethylene nor the propene complex. The pertinent internuclear distance (H to carbonyl C) is ca. 3.05 Å in the ethylene and propylene complexes, but increases to 3.19 Å (center of methyl to carbonyl C) when the hydrogen is replaced by a second methyl substituent in the *trans*-2-butene complex (see Table H in Supporting Information). The distortion in the structure of **4** must be due to the steric demands of the additional methyl substituent (the van der Waals radius of a hydrogen atom is 1.60 Å, whereas the united atom radius of a methyl group is 2.08 Å.[16]

The destabilization of the ring-opened intermediate by the second methyl substituent is an attractive explanation for the anomalously low reactivity (**1** < **7** < **8** in the presence of 2 M BA at 25 °C) of the dinuclear *trans*-2-butene complex **7**. An increase of 3 kcal/mol in the energy of **4** relative to **1** would decrease the equilibrium constant for reaction 2 by over 2 orders of magnitude at 25 °C. Formation of the ring-opened intermediate should be appreciably further uphill from **7** than from the dinuclear ethylene complex **1** or the dinuclear propylene complex **8**.

The existence of an intermediate is necessary in order to explain the anomalous stability of **7** under conditions where the formation of the ring-opened intermediate is reversible. (As shown in Figure 1 of the previous paper,[1] a [BA] of 2 M is well below that—neat BA!—needed to make eq 2 irreversible and its forward step rate-determining.) Any irreversible transformation of the diosmacyclobutanes **1**, **7**, and **8** should reflect the same order of ground-state stabilities observed in the mononuclear reactivity order $Os(CO)_4$(ethylene) < $Os(CO)_4$(propene) (**6**) < $Os(CO)_4$(*trans*-2-butene) (**9**). The second methyl substituent in the dinuclear *trans*-2-butene complex **7** *destabilizes the intermediate more than the ground state* and thus *decreases* the observed reaction rate.

Calculated Secondary Deuterium Kinetic Isotope Effects for C_2H_4 Dissociation. The differences in vibrational force constants between the reactant and the transition state determine the effect of isotopic substitution on the rate of a reaction, and the analogous differences between the reactant and the product determine the corresponding effect on its equilibrium constant. The relationship between kinetic and thermodynamic isotope effects reveals a great deal about the timing (early or late) of the transition state; comparison of these effects has been a valuable tool for the analysis of reactions in which carbon changes its hybridization.[21] Our knowledge of a complete set of vibrational frequencies for **1** and **1**-d_4,[22] along with the literature values for C_2H_4 and C_2D_4,[23] has enabled us to calculate the thermodynamic isotope effect on ethylene dissociation from **1** (**1** vs **1**-d_4)[24] and to predict the maximum kinetic isotope effect expected for a dissociative mechanism (e.g., mechanism I in the previous paper[1]).

The conversion of an isotopically sensitive vibrational mode into a rotational degree of freedom during the fragmentation reaction in eqs 13 and 14 means that the isotope effect upon its equilibrium constant is large,[24] i.e., k_H is appreciably larger than k_D. Division of eq 13 by eq 14 gives eq 15 with an equilibrium constant equal to k_H/k_D—the upper limit for the kinetic isotope effect to be observed if ethylene dissociation is rate-determining.[21]

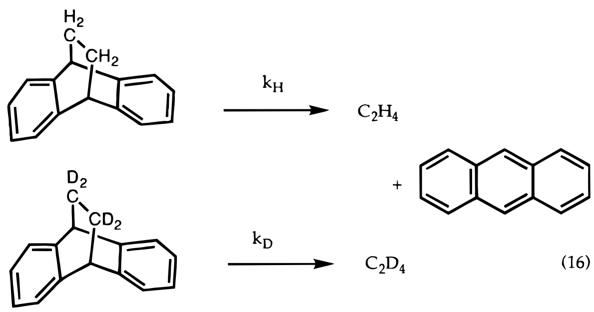


Direct measurement of the equilibrium constant $K_{H/D}$ for eq 15 gives 1.4(1) at 40 °C.[24] Calculation of the same equilibrium constant from the vibrational frequencies and assignments for **1** and **1**-d_4[22] gives 1.4 at 40 °C. Thus 1.4 is the upper limit to the kinetic isotope effect possible for direct dissociation of ethylene from **1**.

The observed KIE for the fragmentation of **1** (1.30(1) at 39 °C with 0.5 M di-*tert*-butyl acetylenedicarboxylate as trap) is not by itself inconsistent with direct dissociation.[25] This isotope effect is only slightly less than that (1.36 at 50 °C)[26] found by Thornton and Taagepera[27] for the retro-Diels−Alder reaction in eq 16—a reaction that surely occurs in a single dissociative step. Although Thornton and Taagepera originally argued that

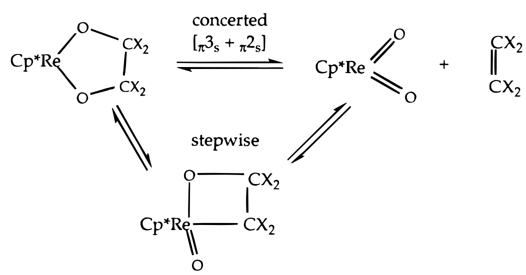
(21) Gajewski, J. J. *Isotopes in Organic Chemistry*; Buncel, E., Lee, E., Eds.; Elsevier: New York, 1987; Vol. 7; Chapter 3, p 121.
(22) Anson, C. E.; Johnson, B. F. G.; Lewis, J.; Powell, D. B.; Sheppard, N.; Bhattacharyya, A. K.; Bender, B. R.; Bullock, R. M.; Hembre, R. T.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1989**, 703.
(23) Duncan, J. L.; Hamilton, E. *J. Mol. Struct.* **1981**, *76*, 65.
(24) Bender, B. R. *J. Am. Chem. Soc.* **1995**, *117*, 11239.
(25) We have not proven that 0.5 M is a sufficient concentration of di-*tert*-butyl acetylenedicarboxylate to achieve a limiting rate. However, Figure 1 in the preceding paper[1] suggests that the limiting rate is reached in neat butyl acrylate, and dimethyl acetylenedicarboxylate is known to displace methyl acrylate from $Os_2(CO)_8$ (Burke, M. R. Ph.D. thesis, U. of Alberta, 1987). At this concentration the observed KIE is plainly far from the inverse one predicted for rate-limiting bridge opening; at higher trap concentrations the carbonyl IR bands are broader, so remeasurement of k_H and k_D would give a less precise KIE.
(26) We note that the KIE measured by Thornton for eq 16 would be slightly greater at the lower temperature of 39 °C.
(27) Taagepera, M.; Thornton, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 1168.

eq 16 had an *early* transition state, subsequent theoretical analysis has established a *late* transition state.[28] KIE values for retro-Diels–Alder reactions have been reviewed.[21]



(16)

The C_2H_4/C_2D_4 isotope effect is also known for the metallacycle reaction, related to the fragmentation of **1**, in eq 17. Gable and Phan measured k_H/k_D for Cp*Re(O)(OCH_2CH_2O) vs Cp*Re(O)(OCD_2CD_2O) as 1.3 at 99.5 °C.[29] (A result equivalent to ours when the temperature difference is considered.) They also examined the analogous extrusion and cycloaddition reactions over a series of olefins with different strain energies. They found that "extrusion of those alkenes which are electronically comparable...show[ed] approximately the same activation enthalpy", while "the range of values" for the activation enthalpy in the reverse direction was "as large as the range of strain energies". After comparing these activation enthalpies Gable and Phan concluded that the left-to-right transition state for eq 17 was *early*, and that the size of their kinetic isotope effect could only be explained by a *multistep* mechanism such as that shown at the bottom of eq 17.[29]

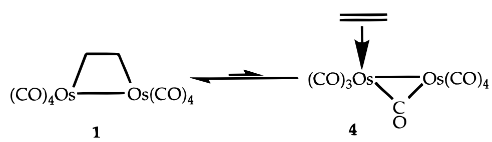


Cp* = η^5-$C_5(CH_3)_5$ X = H, D (17)

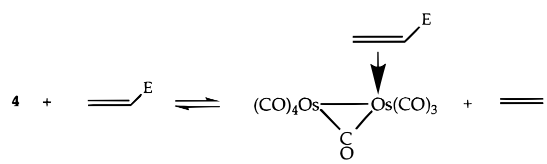
The same explanation—a multistep mechanism—is surely the best explanation for the KIE (1.30(1) at 39 °C) we have measured for the extrusion of olefins from diosmacyclobutanes.[25] That KIE does argue strongly against some mechanisms. We can model **12**, the transition state for the formation of **4** from **1**, with either the osmacyclopropane $Os(CO)_4(C_2H_4)$[30] or Zeise's salt $K[(C_2H_4)PtCl_3]$. The maximum secondary deuterium kinetic isotope effect calculated from the vibrational frequencies and assignments for $Os(CO)_4(C_2H_4)$ and $Os(CO)_4(C_2D_4)$[31] is *inverse*, 0.924 at 40 °C;[32] a similar result, 0.925, is obtained from the frequencies for $K[(C_2H_4)PtCl_3]$ and $K[(C_2D_4)PtCl_3]$.[33] (The *ab initio* calculations above gave a length of 1.406 Å for the C–C bond in **4**, a value between that of a π complex and that of a metallacyclopropane; the distinction is unimportant for calculating the isotope effect because the ethylene C–H bonds are rehybridized to about the same extent in both resonance forms.) Thus ring opening—the formation of **4** from **1**—*cannot* be rate limiting because it cannot explain the observed KIE.

Conclusions

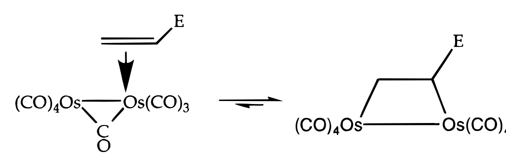
The lack of evidence for ethylene rotation relative to the $Os_2(CO)_8$ framework, and the significant KIE that we have found for the replacement of ethylene by di-*tert*-butyl acetylenedicarboxylate, are ambiguous results—neither proves or disproves the presence of an intermediate. However, the relative stabilities of substituted diosmacyclobutanes can *only* be explained by the reversible formation of an intermediate during olefin/acetylene exchange, and the most plausible intermediate is the ring-opened species **4**. Associative exchange with **4** (eq 18) is consistent with the kinetics in the previous manuscript,[1] and with the retention of stereochemistry observed[34] when substituted olefins are employed. (Coordination of an olefin to a *single* metal, and release of an olefin from that metal, do not affect the pattern of substitution.) The exchange of diosmacyclobutanes with external olefins in eqs 2–19 is *stepwise* but *stereospecific*.



(2)



(18)



(19)

General Implications. A satisfying picture of the formation and fragmentation of metallacycles is beginning to emerge. The exchange reactions of **1** proceed via the ring-opened intermediate **4**, and the exchange reactions of titanacyclobutanes proceed via alkylidene olefin complexes (Scheme 2).[35] Calculations by Upton and Rappé[36] have confirmed this reaction profile—including prior olefin coordination—for the formation of titanacyclobutanes from olefins and titanium alkylidene complexes and have suggested that an empty valence d orbital on the titanium of the alkylidene complex makes olefin coordination possible.

Bennett and Wolczanski have prepared an azametallacyclobutane from the reaction of C_2H_4 with the transient imido

(28) Storer, J. W.; Raimondi, L.; Houk, K. N. *J. Am. Chem. Soc*. **1994**, *116*, 9675.

(29) (a) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1993**, *115*, 3036–3037. (b) Gable, K. P.; Phan, T. N. *J. Am. Chem. Soc.* **1994**, *116*, 833–839.

(30) Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappé, A. K. *Organometallics* **1992**, *11*, 3427.

(31) Anson, C. E.; Sheppard, N.; Powell, D. B.; Bender, B. R.; Norton, J. R. *J. Chem. Soc. Faraday Trans* **1994**, *90*, 1449.

(32) The out-of-plane twisting/tilting mode that becomes a rotational mode when ethylene dissociates from **1** (see ref 24) is preserved during the formation of **4** from **1** ("bridge opening"). Thus the large normal isotope effect calculated for ethylene dissociation from **1** is replaced by an inverse one calculated for isomerization to **4**.

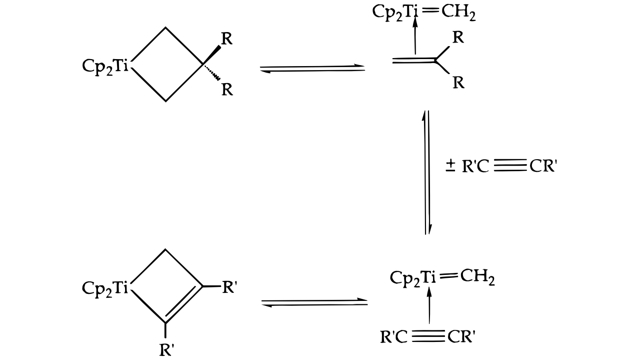
(33) The vibrational assignments for Zeise's salt, $K[(\eta^2\text{-}C_2H_4)PtCl_3]$, have been reported several times (see ref 31). The most complete and reliable assignments have been obtained by inelastic neutron scattering: Jobic, H. *J. Mol. Struct*. **1985**, *131*, 167.

(34) Hembre, R. T.; Ramage, D. L.; Scott, C. P.; Norton, J. R. *Organometallics* **1994**, *13*, 2995.

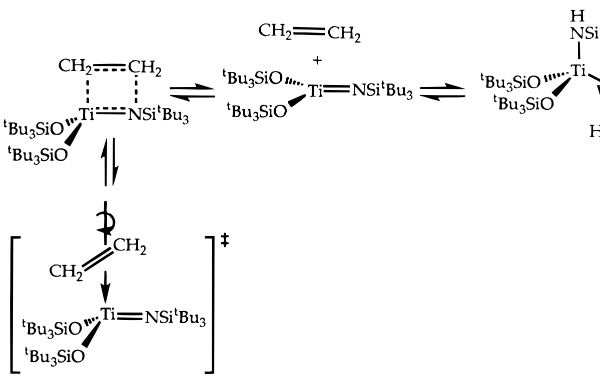
(35) (a) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880–4890. (b) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406–2413. (c) Hawkins, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2821–2823.

(36) Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

Scheme 2. Exchange Reactions of Titanocyclobutanes



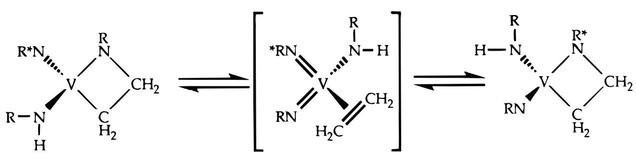
complex $(silox)_2Ti{=}NSi^tBu_3$; the ethylene unit *rotates* relative to the Ti/N framework, against a barrier of only 8.9 kcal/mol (eq 20).[37] (The two methylenes of the C_2H_4 ligand are



(20)

equivalent in the ^1H NMR at 20 °C, but separate multiplets are observed when the sample is cooled to −130 °C.)

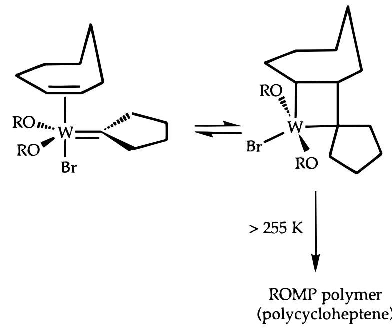
Similar rotation of the ethylene (i.e., relative to the V/N framework) has been observed by Horton and co-workers in the vanadaazetine system in eq 21.[38]



(21)

Earlier, Kress and Osborn prepared the alkylidene cycloheptene complex in eq 22 at low temperatures.[39] The complex catalyzed the metathesis and polymerization of cycloheptene above 255 K, implying that such alkylidene olefin complexe are intermediates in metathesis. A density functional study by Ziegler and Folga[40] of the formation of molybdacyclobutanes from Mo alkylidene complexes suggests that initial olefin attack is at the metal, forming an alkylidene olefin intermediate.

It is tempting to suggest that apparent 2 + 2 organometallic cycloadditions always involve initial coordination of one partner to the metal in the other partner. This coordination requires an empty orbital. Rather than describing the reaction as 2 + 2, it may be preferable to use the notation "2 + 2 + 0", the "0" denoting the need for an empty orbital. Rappé and Upton have



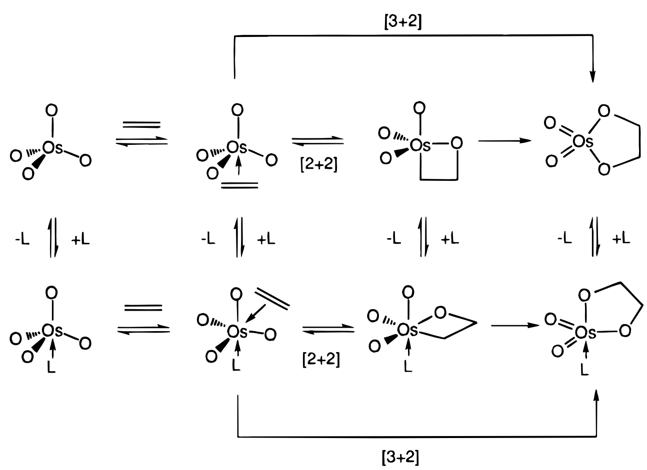
(22)

already suggested[41] that the factor critical for low barriers in 2 + 2 reactions is the presence of an empty valence orbital (p or d) on one of the reacting partners; this empty valence orbital can serve as either a σ (Lewis acid/base) or a π acceptor for the other partner.

This idea has important implications for the formation of osmate esters during the dihydroxylation of alkenes, a reaction that is particularly important when carried out asymmetrically and catalytically in the presence of an optically active ligand L.[42] Sharpless and co-workers prefer[42,43] a metallaoxetane [2 + 2] pathway; as evidence for at least two enantioselective steps they point to the observation of two linear regions with different slopes in plots of ln (product ratio) vs T^{-1}.[43a] Corey and co-workers prefer initial coordination of the alkene to the osmium of the OsO_4, followed by a [3 + 2] cycloaddition; as evidence they point to their ability to explain the stereochemical outcomes produced by various chiral ligands.[44]

The results of Phan and Gable[29] (eq 17) imply that osmate esters are *not* formed by direct 3 + 2 cycloadditions between OsO_4 and olefins. Nugent has spectroscopically characterized an OsO_4/alkene complex, observable prior to osmate ester formation.[45] Veldkamp and Frenking have calculated that coordination of an alkene is energetically possible before a [2 + 2] reaction with OsO_4 (at least when there is only one coordinated ligand L).[46]

The above observations *and* the fact that our diosmacyclobutane **1** is formed from the ring-opened intermediate **4** suggest that an osmaoxetane is formed from the analogous polyoxo/alkene complex (eq 23).

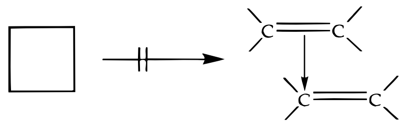


(23)

We close by considering why all-carbon four-membered rings cannot revert to olefins by a stepwise, stereospecific, mechanism of this sort. *The ring must contain at least one element that can rehybridize to give an empty orbital as an acceptor for the departing double bond*. Cyclobutane does not have the luxury of the mechanism in eq 24, and must resort to a *diradical*

(37) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179−2180.
(38) de With, J.; Horton, A. D.; Orpen A. G. *Organometallics* **1993**, *12*, 1493−1496.
(39) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585−1587.
(40) Folga, E.; Ziegler, T. *Organometallics* **1993**, *12*, 325.
(41) Rappé, A. K.; Upton, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 7507.

intermediate instead.[34]



(24)

Experimental Section

Syntheses of starting materials, purification of solvents and reagents, instrumentation, and the collection and analysis of kinetic data were described in the previous paper.[1] ($^{13}CH_2CH_2$)$Os_2(CO)_8$ was prepared as previously reported.[30] $Os(CO)_4(C_2D_4)$ and $Os_2(CO)_8(C_2D_4)$ were prepared in the same way as the analogous complexes of unlabeled ethylene;[15,47] details are given in Supporting Information.

(η^2-CH_2CHCH_3)$Os(CO)_4$ (6) and (μ-η^1,η^1-CH_2CHCH_3)$Os_2(CO)_8$ (8). A brief synthesis of $Os_2(CO)_8$(propene) (**8**) has been published.[3] The propylene adducts can be prepared by the same procedure as the ethylene adducts,[15,47] but more care must be taken to avoid decomposition during isolation. In a typical reaction, 300 mg of $Os_3(CO)_{12}$ was slurried in 250 mL of CH_2Cl_2 in a 500 mL Fischer & Porter pressure vessel. The vessel was charged with 20 psig propylene, vented once (in a hood), and allowed to equilibrate for a few minutes. The vessel was then placed next to an $NaNO_2$-filtered light source and photolyzed for approximately 12 h. Then, as quickly as possible because of the instability of **8**, the pressure vessel was vented, its contents were transferred to a 500 mL flask, and the solvent was removed under reduced pressure. The propylene adducts **6** and **8** were separated on a Chromatotron as described[15] for the ethylene complexes. The first band contained **6** and was collected in a high-vacuum bulb. The second band contained the dinuclear adduct **8**; solvent removal at 0 °C gave 100−150 mg (50−70%). (Because **8** is unstable at room temperature in solution and as a solid, it is isolated in lower yield than **1**.) For **8**: IR (pentane) 2121 (vw), 2076 (s) 2037 (m), 2031 (vs), 2021 (m), 2009 (s), 1994 (m) cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2, −20 °C) δ 1.16 (dd, 1H, $^2J_{gem}$ = −9.9(5) Hz, $^3J_{trans}$ = +13.2(5) Hz), δ 1.56 (d, 3H, $^3J_{HH}$ = +6.9 Hz), δ 1.96 (m, 1H, $^3J_{cis}$ 7.6(5) Hz, $^3J_{trans}$ 13.2(5) Hz and $^3J_{HH}$ +6.9 Hz), δ 2.12 (dd, 1H, $^2J_{gem}$ −9.9(5) Hz and $^3J_{cis}$ +7.6(5) Hz); ^{13}C NMR (75.47 MHz, CD_2Cl_2, −20 °C) δ −13.2, *C*H_2; δ −7.1, *C*H; δ 36.7, *C*H_3.

The mononuclear propylene complex **6** can be isolated in 75% theoretical yield by low-temperature vacuum fractionation as described for (η^2-C_2H_4)$Os(CO)_4$.[30] For (η^2-CH_2CHCH_3)$Os(CO)_4$ (**6**): IR (pentane) 2105 (w), 2016 (vs), 1986 (s) cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.81 (dd, 1H, $^2J_{gem}$ = −2.6 Hz, $^3J_{trans}$ = 11.0 Hz); δ 2.04 (d, 1H, $^3J_{HH}$ = +6.1 Hz); δ 2.15 (dd, 1H, $^2J_{gem}$ = −2.6 Hz, $^3J_{cis}$ = +8.3 Hz); δ 2.78 (m, 1H, $^3J_{cis}$ = +8.3 Hz, $^3J_{trans}$ = +11.0 Hz, $^3J_{HH}$ = +6.1 Hz).

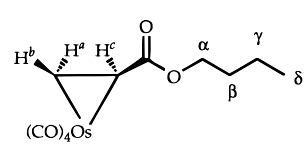
***trans*-2-Butene Adducts 7 and 9.** When *trans-2*-butene was used under the same conditions, a color change was not observed; instead a precipitate formed which accumulated at longer reaction times. If the photolysis was stopped after several hours (before all the color had disappeared), both mono- and dinuclear adducts were present and could be isolated in low yields. For (μ-η^1,η^1-*trans*-$CH_3CHCHCH_3$)$Os_2(CO)_8$ (**7**): IR (pentane) 2119 (vw), 2075 (s), 2036 (m), 2019 (vs), 2020 (m), 2008 (s), 1990 (m br), 1990 (wsh) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, −20 °C) δ 1.57 m (6H); δ 1.75 (m, 2H), $^3J_{trans}$ = +12.2(8) Hz, $^3J_{CH-CH_3}$ = +7.0(8) Hz). For (η^2-*trans*-$CH_3CHCHCH_3$)$Os(CO)_4$ (**9**): IR (pentane) 2105 (w), 2013 (vs), 1982 (m br) cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.77(m, 2H), δ 2.02 (m, 6H, $^3J_{trans}$ = 10.5(2) Hz, $^3J_{H-CH_3}$ = 6.5(2) Hz).

($^{13}CH_3$)$_2Os_2(CO)_8$ was prepared from $^{13}CH_3I$ and $Na_2[Os_2(CO)_8]$. Benzophenone (288 mg, 1.58 mmol) and freshly cut Na (44 mg, 1.91 mmol) were weighed out in an inert atmosphere box and placed in a flask with a glass-covered stirbar. Freshly distilled THF (75.0 mL) was added to give a bright blue 2.11 × 10^{-2} M solution of Na/Ph_2CO. $Os_2(CO)_8(C_2H_4)$ (**1**) (100 mg, 1.58 mmol) was placed in a separate flask, THF (15 mL) was added, and the solution was chilled to 0 °C. The ketyl solution was added dropwise to the colorless solution of **1** over 10 min; the solution remained homogeneous and turned yellow/orange, while IR showed bands for $Na_2[Os_2(CO)_8]$[48] and Ph_2CO. Excess (0.25 mL) $^{13}CH_3I$ (99% ^{13}C) was added and the solution was stirred at ambient temperature for 6 h. The THF was removed at reduced pressure, and the yellow/orange residue was extracted with pentane, spotted on a Chromatotron plate and eluted with pentane; IR (pentane) showed ν(CO) bands identical to those of $Os_2(CO)_8(CH_3)_2$.[49] The pentane was removed at reduced pressure (0 °C) to give $Os_2(CO)_8$-($^{13}CH_3$)$_2$ as a white solid (yield 35 mg, 0.55 mmol, 35%): ^{1}H NMR (CD_2Cl_2) δ 0.1 (d, $^1J_{CH}$ = 130.2 Hz, 6H); ^{13}C NMR (CD_2Cl_2) δ −41.9 (q, $^1J_{CH}$ = 130.2 Hz), 182.1 (4CO_{ax}), 173.2 (d, $^2J_{CC}$ = 11.6 Hz, 2CO_{eq}), 167.7 (2CO_{eq}).

Variable-Temperature ^{13}C NMR Experiments. Two 10 mg samples of **1**-^{13}C were added to separate 5 mL NMR tubes. C_6D_6 or CD_2Cl_2 (0.6 mL) was added by vacuum transfer to give an 0.03 mM solution, and the tube was sealed under vacuum. {^{1}H} ^{13}C NMR were measured from −20 to 25 °C (CD_2Cl_2) or from 25 to 60 °C (C_6D_6), on an IBM WP 200 SY (75.47 MHz) spectrometer.

Kinetics of the Reactions of $Os_2(CO)_8$(alkene) and $Os(CO)_4$-(alkene) with BA. In a typical experiment a stock solution (8.61 mM) of $Os_2(CO)_8$(*trans*-2-butene) (**7**) in decane was prepared. To 4.5 mL of this stock solution was added BA (1292.6 mg, 10.085 mmol), and the solution was diluted with decane to 10.0 mL in a volumetric flask ([BA] = 2017.0 mM, [**7**] = 3.87 mM; [BA]:[**7**] = 521:1). The tube was placed in a 35.0 °C bath and the reaction was monitored for 433.1 min; a complete description of the collection and analysis of kinetic data is in the preceding paper. The global rate constant of the experiment just described was 1.011(13) × 10^{-4} s^{-1}.

$Os(CO)_4$(BA) (10). It was impractical to isolate **10** from the decane solutions used in kinetic studies of the reaction **4** + BA → **10** (at >1 M BA). Therefore, **10** was prepared along with the dinuclear BA complex **3** by photolysis of a CH_2Cl_2 slurry of $Os_3(CO)_{12}$ and BA. Mononuclear **10** was chromatographed with pentane and vacuum distilled with difficulty to give a yellow liquid. Attempts to obtain a satisfactory analysis for **10**, which appeared pure by IR, ^{1}H NMR, and MS, failed because the yellow impurity could not be removed: IR (pentane) 2124 (w), 2045 (vs), 2029 (s), 1999 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) 4.13 (m, 1H, $^2J_{HH}$ = −11.5 Hz, $^3J_{HH}$ = 6.8 Hz, diastereotopic α-CH_2), 3.93 (m, 1H, $^2J_{HH}$ = −11.5 Hz, $^3J_{HH}$ = 6.8 Hz, diastereotopic α-CH_2), 2.66 (dd, 1H, H^c), 2.20 (dd, 1H, H^b), 1.55 (dd, 1H, H^a), 1.43 (m, 2H β-CH_2), 1.23 (m, 2H, γ-CH_2), 0.78 (t, 3H, δ-CH_2) ppm. Its mass spectrum (EI) showed a peak for the molecular ion at *m/e* 432 with the appropriate isotopic distribution.



Alkene Exchange with $Os(CO)_4$(alkene). Formation of Os_2-$(CO)_8$BA (3). An aliquot (1.0 mL) of a stock solution (0.146 M) of $Os(CO)_4$(propene) (**6**) was diluted with decane (∼5 mL) and BA was

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added (265.0 mg, 2.068 mmol). The resulting solution was diluted to 10 mL ([BA] = 206.8 mM, [**6**] = 14.6 mM; [BA]:[**6**] = 14.2). The tube was placed in a 65.0 °C bath and the reaction was monitored for 239.2 min; for a the collection and analysis of kinetic data see the preceding paper.[1] A small peak that grew in at 2085 cm^{-1} suggested the presence of **3**. Isosbestic points were not observed.

In an effort to increase the amount of **3**, the reaction was repeated with [BA] = 31.6 mM, [**6**] = 29.2 mM ([BA]:[**6**] = 1.08). A plot of absorbance vs time, measured at two peaks each of **6** and **3**, is presented in Figure B of Supporting Information. Subtraction of the spectrum of $Os(CO)_4$BA (**10**) from the spectrum of the reaction at infinity left peaks (2085 (vs), 2046 (m), 2037 (vs), 2027 (s), 2015 (s), 1999 (s) cm^{-1}) that agreed with those assigned to **3** in the previous manuscript;[1] subtraction also gave a peak corresponding to the most intense peak of $Os_3(CO)_{12}$ (2070 cm^{-1}). (The spectra resulting from substraction are shown in Figure A in Supporting Information.)

To obtain concentration vs time profiles for analysis with GEAR/GIT, the reaction was repeated with [BA] = 5.46 mM and [**6**] = 4.80 mM ([BA]:[**6**] = 1.14). The tube was placed in a 65.0 °C bath, and the reaction was monitored for 285.94 min. The known molar absorptivities (Table A in Supporting Information) were used to calculate the concentrations of Os−carbonyl species from the measured absorbances at various wavelengths. (Suitable software was available as part of our IR operating system, from On-Line Instrument Systems, Jefferson, GA.) The calculated concentrations are given in Table B in Supporting Information and are plotted vs time in Figure 3. The resulting mole fractions of total osmium (in terms of total Os) are given vs time in Table C in Supporting Information.

Measurement of the Kinetic Deuterium Isotope Effect. A mixture of approximately 50 mg (7.6 mM) of **1** and 50 mg (7.6 mM) of **1**-d_4 in dodecane (20 mL) was heated (39 °C) in the presence of a large excess (2.26 g, 0.5 M) of DTBAD; details are given in Supporting Information. The kinetic isotope effect was calculated from eqs 25 and 26; R_s (the C_2D_4/C_2H_4 ratio from the starting material remaining at a given time), R_p (the C_2D_4/C_2H_4 ratio of the product at that time), and R_o (the C_2D_4/C_2H_4 ratio from the amount of both reactants initially present) were measured directly by GC−MS; the extent of reaction, $1 - F_H$, was calculated from the observed decrease in absorbance for the 2076 cm^{-1} IR band common to both **1**-d_4 and **1**. Equation 25 gave 1.29 as the KIE, while eq 26 gave 1.30 as the KIE.

Computational Details. Geometries for the parent diosmacyclobutane (**1**) as well as the corresponding transition state (**12**) and intermediate (**4**) coordinates were calculated using analytic gradients

$$\frac{k_H}{k_D} = \frac{\log(1 - F_H)}{\log[(1 - F_H)(R_s/R_o)]} \tag{25}$$

$$\frac{k_H}{k_D} = \frac{\log(1 - F_H)}{\log\left[1 - \frac{F_H R_p}{R_o}\right]} \tag{26}$$

and a Hartree−Fock wave function. Effective core potentials were used on carbon, oxgyen, and osmium. For carbon and oxygen the effective core potentials of Stevens, Basch, and Krauss[50] were used to replace the 1s electrons. For osmium the Hay and Wadt[51] effective potential was used to replace the core orbitals up through $n = 4$. For hydrogens a scaled basis was used.[52] For osmium the basis given by Hay and Wadt[51] was used. For carbonyl carbon and oxygen the molecularly contracted basis listed in Table D of Supporting Information was used. For the olefin carbon atoms the basis reported previously[30] was used.

Molecular mechanics minimizations were done with the Dreiding force field[16] augmented with parameters for Os. Minimizations were performed by Biograf[53] Version 2.2, using a congugate gradient technique with the carbon, osmium, and oxygen atoms of the $Os_2(CO)_8$ fragment constrained to the *ab initio* geometry. The Os van der Waals parameters used are $R = 3.00$ Å, $\epsilon = 0.055$ kcal. Coordinates for **1**, **12**, and **4**, as well as for their propyl and *trans*-2-butenyl analogs, are given in Supporting Information.

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Supporting Information Available: IR extinction coefficients and spectrum subtraction (1 page), kinetics of **6** and BA (9 pages); basis sets, results of calculations, coordinates for molecular mechanics (14 pages); kinetic isotope effect measurements (5 pages). (29 pages total). See any current masthead page for ordering and Internet access instructions.

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