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DIOSMACYCLOALKANES AS MODELS FOR THE FORMATION OF HYDROCARBONS FROM SURFACE METHYLENES

Progress Report

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I. Report of Progress to Date

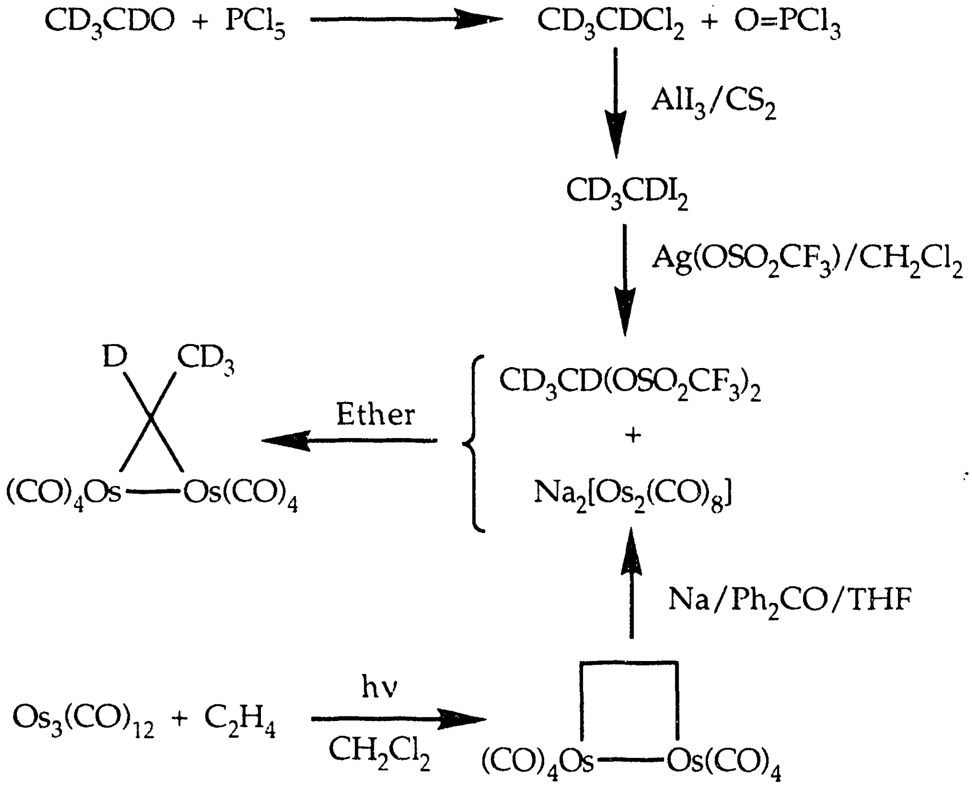
Department of Energy (Grant #FG02-84ER13299)
Jack R. Norton, Principal Investigator

A. Vibrational Models for Surface Ethylidenes

A manuscript describing this work is now being assembled by C. Anson and N. Sheppard, our collaborators at the U. of East Anglia (UK). Both groups have written their contributions, and the final manuscript will have been submitted for publication by the time this proposal is reviewed.

Goal: a vibrational "fingerprint" of CH_3CH so that it can be identified on metal catalyst surfaces

We have developed the following method for the preparation of $CH_3CD(OTf)_2$ and $CD_3CD(OTf)_2$, and have used these labelled geminal ditriflates for the preparation of $Os_2(CO)_8(\mu\text{-}CDCH_3)$ and $Os_2(CO)_8(\mu\text{-}CDCD_3)$.



In collaboration with Anson and Sheppard we have obtained low-temperature infrared and Raman spectra of these labelled diosmacyclopropanes and used them to assign the vibrational modes of the bridging ethylidene ligands (Table I). After comparison with the well-established vibrational assignments for CH_3CHX_2[1] the assignments of the diosmacyclopropane modes are unequivocal, although the CD_3CD modes identified with an asterisk are strongly coupled.

Table I. The positions (cm^{-1}), relative infrared intensities, isotopic ratios and vibration/symmetry assignments for the infrared and Raman bands of [μ_2-CHCH$_3$)Os$_2$(CO)$_8$)], d^0, d^1 and d^4.

(CH_3CH)		(CH_3CD)		(CD_3CD)		Isotopic Ratios		Assignment	Symmetry
IR	Ra	IR	Ra	IR	Ra	(CH_3CH)/(CH_3CD)	(CH_3CH/(CD_3CD)		
					2242(w)			2 x δCD_3 *as*	A''
2950(s)	2950(mw)	2945(s)	2948(mw)	2206(ms)	2207(m)	1.00	1.337	$\nu CH_3/CD_3$ *as*	a',a''
2926(w)		2926(w)						2 x δCH_3 *as*(F.R.)	A'
2916(ms)	2919(s)	2184(m)	*ca.* 2190(ms)	2187/3(m)	2186(m)	1.335	1.334	$\nu CH/CD$	a'
2905(m)	*ca.* 2910(sh)	2907(m)	2911(ms,sh)			1.00		2 x $\delta CH_3/CD_3$ *as*(F.R.)	A'
2878(w)	2883(mw)	2877(m)	2878(m)	2170(w)	obs.	1.00	1.328	2 x $\delta CH_3/CD_3$ *as*	A''
2850/48(ms)	2860/52(m)	2847(s)	2847(s)	obs.	obs.	1.00		$\nu CH_3/CD_3$ *s* (F.R.)	a'
2714(w)	2715(w)	2715(w)	2714(w)	obs.	2062(mw)	1.00	1.317	2 x $\delta CH_3/CD_3$ *s*	A'
1447(ms)	1450(m)	1447(ms)	1449(m)	1123(ms)	1121(m)	1.00	1.291	$\delta CH_3/CD_3$ *as*	a'
1447(ms)	1450(m)	1447(ms)	1449(m)	1052(ms)	1054(m)	1.00	1.375	$\delta CH_3/CD_3$ *as*	a''
1369(m)	1371(w)	1368(m)	1370(w)	1037(w)		1.00	1.338	$\delta CH_3/CD_3$ *s**	a'
1302(ms)	1303(w)	1120(ms)	1121(w)	932/24(vw)	928(w)	1.163	1.403	$\delta CH/\delta CD$*	a'
1053(mw)	-	1054(w)	-	1023(m)	1023(m)	1.00	1.029	CH_3 rock/νCC*	a'
1030(s)	1035(m)	1024/1(s)	1023(mw)	845(s)	845(s)	1.006	1.219	CH_3/CD_3 rock	a''
989/4(m)	989(m)	846/37(vw)	841(mw)	757/51(mw)	757(ms)	1.175	1.306	$\nu CC/CD_3$ rock*	a'
952/45(m)	945(w)	713(m)	712(m)	691/87(mw)	689(mw)	1.331	1.377	$\gamma CH/CD$	a''
545(w)	545(ms)	537(ms)	535(ms)	525(m)	*ca.* 520(m,sh)	1.017	1.038	νOsC *as*	a''
448(s)	445(ms)	432(ms)	438(ms)	434(ms)	431(ms)	1.028	1.032	νOsC *s*	a'
	312(m)		309(m)		286(m)	1.010	1.091	δOs_2C_2 *s*	a'
	196(m)		195(m)		*ca.* 176 (sh)	1.005	1.115	δOs_2C_2 *as*	a''
	155(vs)		155(vs)		155(vs)	1.000	1.000	$\nu OsOs$	a'

(F.R.) - Fermi Resonance of 2 x $\delta CH_3/CD_3$ *as* with $\nu CH_3/CD_3$ *s*; obs.-band obscured by strong carbonyl νCO bands. IR- infrared; Ra- Raman. Additional IR/Ra bands that are virtually unaffected by isotopic substitution are assumed to be carbonyl δM-CO and νM-CO bands, *viz.* 616(m,IR;w,Ra); 605 (vs,IR); 592 (vs,IR;w,Ra); 583 (s,IR); 562(s,IR;w,Ra); 495/90 (m,IR;vs,Ra); (470,m,sh,Ra); 455(s,IR); 423 (s,IR;w,Ra); 390 (m,Ra)

Other very weak features assumed to be δM-CO/νM-CO overtones or combinations, *viz.* (CH_3CH) 1110, 1070; (CH_3CD), 1108, 1065, 1041, 992; (CD_3CD) 1070,991.

*These group modes of the (CD_3CD) compound are strongly coupled.

Previously reported surface ethylidenes[2] have turned out to be ethylidynes (CH_3C).[3] The information in Table I should enable the identification of an ethylidene species on the surface of a catalyst. Two apparent examples, shown in Table II, arise from (1) the adsorption of ethylene onto Pt(111) with preadsorbed oxygen,[3c] and (2) hydrogenation of CO adsorbed on Rh/Al_2O_3.[4]

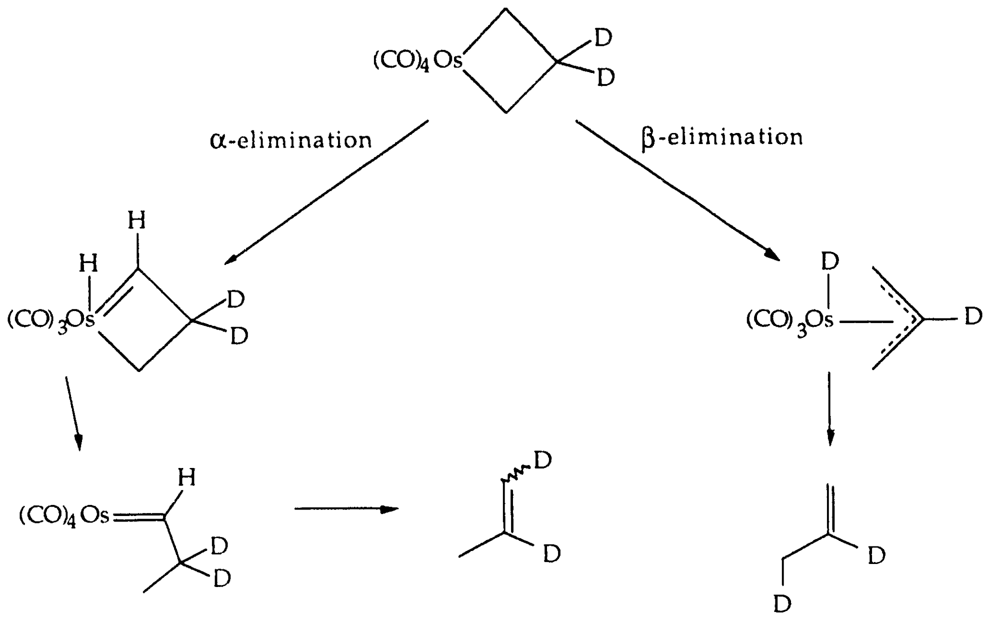
Table II. The assigned fundamentals (cm-1) for the ethylidene groups in several metal coordination compounds and for possible ethylidene species on metal surfaces

$(\mu_2\text{-CDCD}_3)\text{Os}_2(\text{CO})_8$		$(\mu_2\text{-CHCH}_3)\text{Os}_2(\text{CO})_8$	$CO/H_2/$ Rh/Al_2O_3	$C_2H_4/$ Pt(111)/O
	a′ modes			
2207	$\nu CH_3/CD_3$ *as*	2950	2964(s,b)	2980 (ms,b)
2187	$\nu CH/CD$	2918	2916(s,b)	
-	$\nu CH_3/CD_3$ *s*	2847		
1123	$\delta CH_3/CD_3$ *as*	1449	1463(ms)	1460(s)
1037	$\delta CH_3/CD_3$ *s*	1369	1378(m)	1380 (ms,vb)
1023	$\delta CH/CD$ *ip*	1302	1256(m)	1380 (ms,vb)
928	$\rho CH_3/CD_3$	1053	1058(m)	
757	νCC	989	940(mw)	940(m)
434	νOsC *s*	448		480 (vs)
286	$\delta CCOs$ *s*	312		300(m)
155	$\nu OsOs$	155		
	a″ modes			
(2207)	$\nu CH_3/CD_3$ *as*	(2950)		
1054	$\delta CH_3/CD_3$ *as*	(1449)		
845	$\rho CH_3/CD_3$	1030		
689	$\delta CH/CD$ *oop*	945		
525	νOsC *as*	545	594 (ms)	
ca 176	$\delta CCOs$ *oop*	196		

B. "Alpha vs. Beta Hydrogen Elimination in the Formation of Propene from an Osmacyclobutane", W. Fischer, R.T. Hembre, D.R. Sidler, and J.R. Norton, *Inorg. Chim. Acta,* 1992, *198-200,* 57.

Question to be Answered: does α-elimination play a role in the fragmentation of metallacyclobutanes?

We have examined the fragmentation of the osmacyclobutane below in a gas-phase flow system. We have found the only product to be propylene, with no evidence for the cyclopropane Lindner[5] has reported. Control experiments have shown that the deuterium content and distribution of propylene remain unaffected after it is formed. Over half the propylene is formed by the expected β elimination. However, the formation of a significant amount of $CH_3CD{=}CHD$ shows that, contrary to the conventional wisdom, *some α elimination is occurring.*



C. Mechanism of the formation and fragmentation of diosmacyclobutanes.

Publications that have appeared during 1990-93:

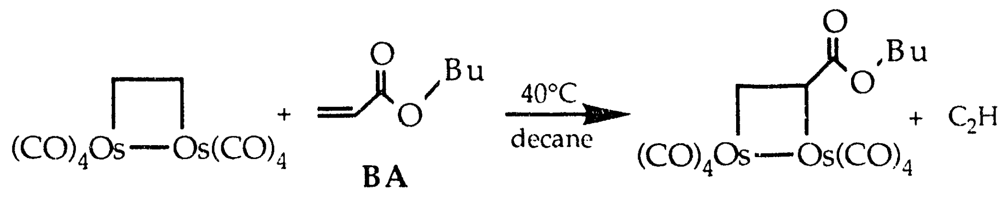
(a) "The Photochemistry of Dinuclear Osmium Carbonyl Complexes; Characterization of $Os_2(CO)_8$ Using Matrix Isolation", A. Haynes, M. Poliakoff, J.J. Turner, B. Bender and J.R. Norton, *J. Organomet. Chem.* **1990**, *383*, 497.

(b) "A Single Crystal Neutron Diffraction Study of (μ–η^1, η^1–C_2H_4)$Os_2(CO)_8$, A Model for One Type of Chemisorbed Ethylene", O.P Anderson, B.R. Bender, J.R. Norton*, A.C. Larson*, and P.J. Vergamini, *Organometallics* **1991**, *10*, 3145.

Two additional publications based on the material below are in draft form. Additional publications are in preparation describing (1) the structure of (μ-C_2H_4)$Os_2(CO)_8$ in a nematic phase solvent, and (2) evidence that ethylene in diosmacyclobutanes does not rotate prior to exchange, as well as H/D isotope effects on their exchange.

Goal: (long-term) understanding the factors that determine stereochemistry during metallacycle formation and cleavage; (immediate) explaining why the loss of olefins from (μ-olefin)$Os_2(CO)_8$ is stereospecific when that from the analogous cyclobutane is not.

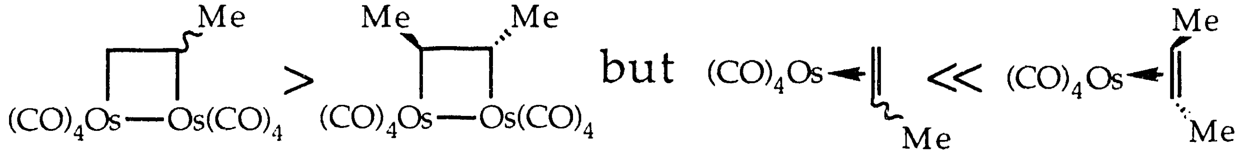
An example of olefin exchange by a diosmacyclobutane is shown below.

 (1)

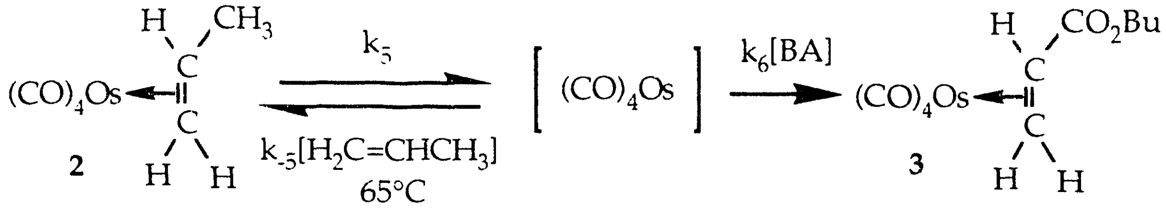
Any proposed mechanism must explain the high stereospecificity observed in these reactions[6] in contrast to the complete loss of stereochemistry in the fragmentation of the isolobal cyclobutane.[7]

Four possible mechanisms are shown on the following page. We have ruled out **mechanism IV** (simple associative) in view of the observation of saturation behavior as [BA] is increased. **Mechanism I** (simple dissociative) is an apparent violation of the symmetry rules for cycloadditions. **Mechanisms II** and **III** involve a "ring-opened" species **1** that we (publication a̲ above) and others[8] have seen in matrix isolation and transient IR experiments. As olefins coordinated to a single metal are known to exchange stereospecifically, the involvement of **1** offers an attractive explanation of the stereospecificity of these exchange reactions. Mechanisms analogous to **II** and **III** have been proposed by Anslyn and Grubbs[9] for titanacyclobutane cleavage; **1** is isolobal to the alkylidene olefin complexes they propose as intermediates.

Some evidence in favor of the intermediacy of **1** is offered by looking at exchange rates as a function of the departing olefin. The propene adduct of $Os_2(CO)_8$ undergoes exchange more rapidly than the *trans*-2-butene adduct! This observation is contrary to the normal rules of olefin complex stability[10]



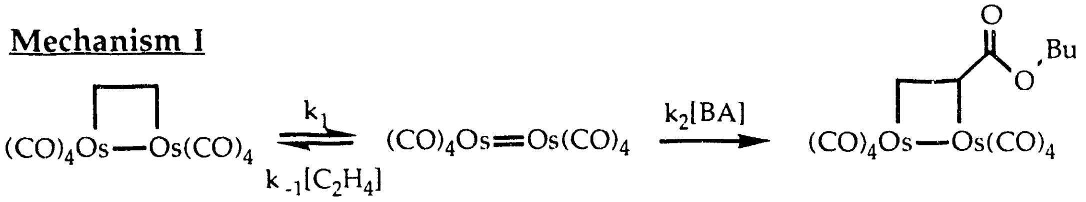
as exemplified by the mononuclear Os olefin complexes shown above. We have confirmed that the olefin dissociation rate constant k_5 is much faster for $Os(CO)_4$(*trans*-2-butene) than for $Os(CO)_4$(propene). (We observe the saturation behavior expected for the mechanism shown — a mechanism analogous to that established for the analogous tetracarbonyl iron olefin system.[11])



(2)

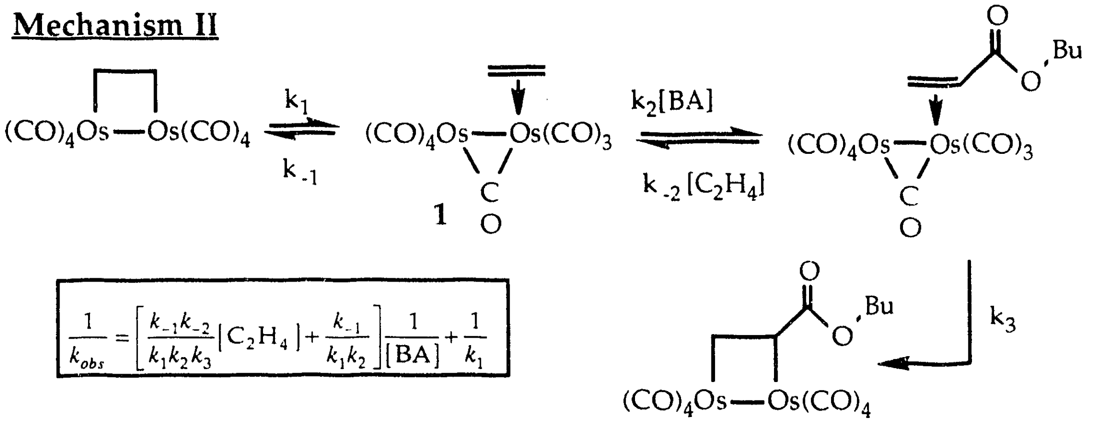
We attribute the anomalous stability of the $Os_2(CO)_8$(*trans*-2-butene) adduct to unfavorable steric interactions in the ring-opened intermediate **1**. This is consistent with the results of molecular modeling studies performed in collaboration with Professor Anthony K. Rappé at CSU. Those studies indicate that the *trans*-2-butene version of **1** is destabilized at least 3 kcal/mol relative to its ethylene and propene analogs, due to close contact between the interior methyl group and a carbonyl on the adjacent Os atom (see page 7). This destabilization leads to relatively lower concentrations of the intermediate **1**, and lower overall rates of exchange, in the *trans*-2-butene case.

Mechanism I



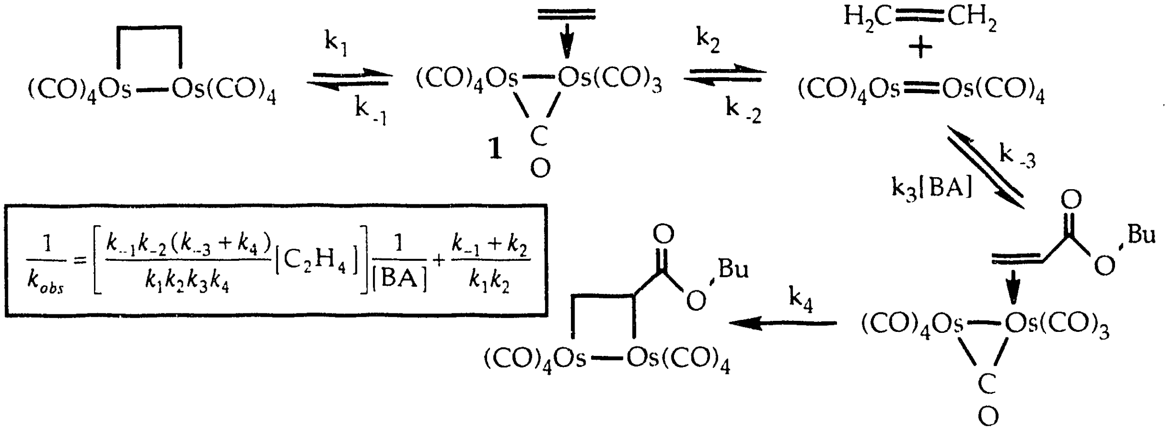
$$\frac{1}{k_{obs}}=\left[\frac{k_{-1}}{k_1k_2}[C_2H_4]\right]\frac{1}{[BA]}+\frac{1}{k_1}$$

Mechanism II



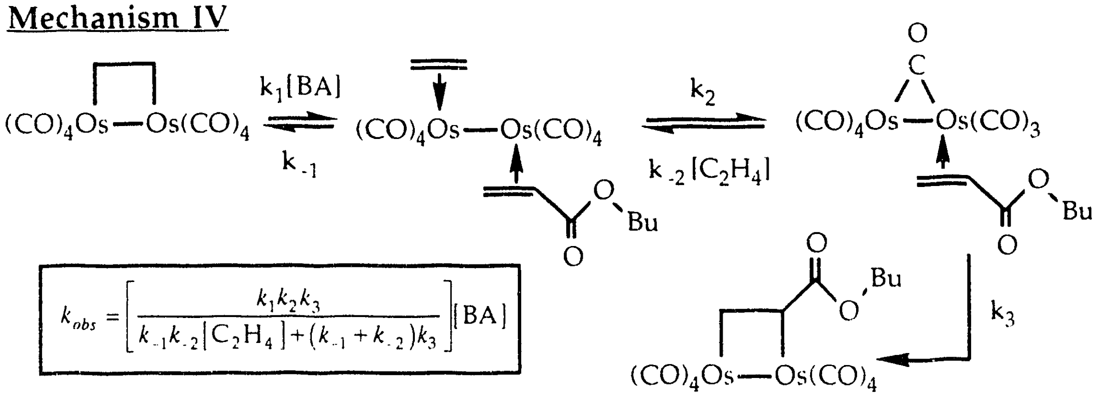
$$\frac{1}{k_{obs}}=\left[\frac{k_{-1}k_{-2}}{k_1k_2k_3}[C_2H_4]+\frac{k_{-1}}{k_1k_2}\right]\frac{1}{[BA]}+\frac{1}{k_1}$$

Mechanism III

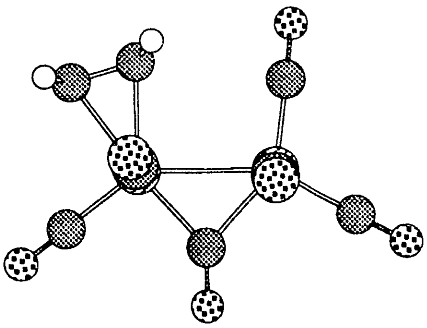


$$\frac{1}{k_{obs}}=\left[\frac{k_{-1}k_{-2}(k_{-3}+k_4)}{k_1k_2k_3k_4}[C_2H_4]\right]\frac{1}{[BA]}+\frac{k_{-1}+k_2}{k_1k_2}$$

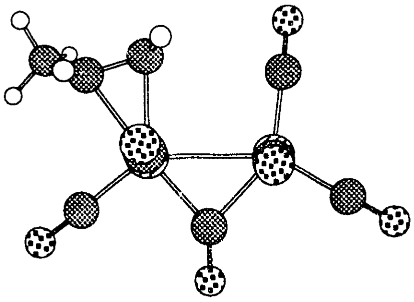
Mechanism IV



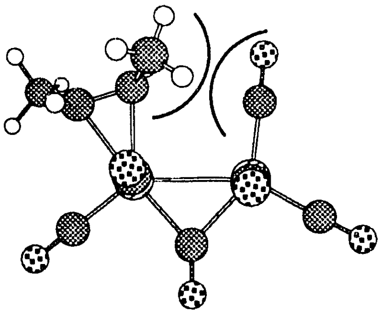
$$k_{obs}=\left[\frac{k_1k_2k_3}{k_{-1}k_{-2}[C_2H_4]+(k_{-1}+k_{-2})k_3}\right][BA]$$



1-ethylene



1-propene



1-*trans*-2-butene

We have found that diosmacyclobutane exchange reactions like (1) proceed by the ring-opening/associative exchange mechanism: **mechanism II**. Both **mechanisms II** and **III** predict that a plot of $1/k_{obs}$ *vs.* [BA] at constant [C_2H_4] should yield a straight line, the slope of which should show positive [C_2H_4] dependence. Such slopes must be related to [C_2H_4] by one of the following equations, if **mechanism II** or **III** is operative. Thus, if the slope from a $1/k_{obs}$ vs. [BA] plot is plotted *vs.* [C_2H_4], a nonzero intercept should be obtained if **mechanism II** is the operative mechanism and a zero intercept otherwise.

Mechanism II

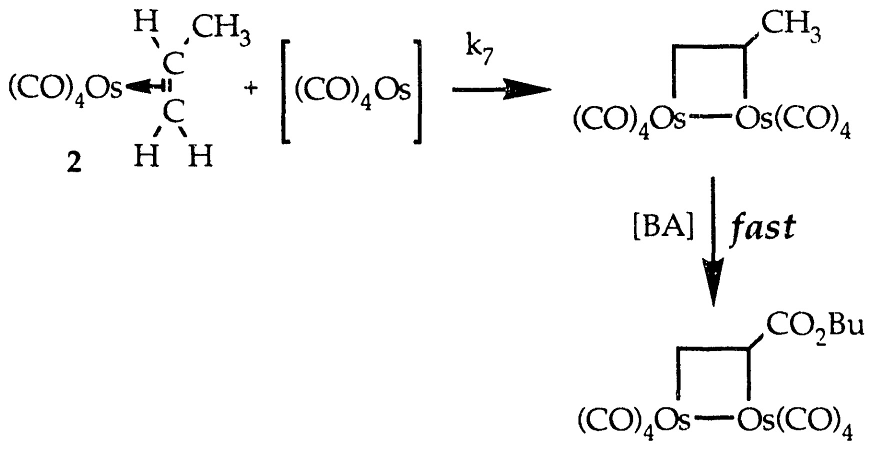
$$slope = \left[\frac{k_{-1}k_{-2}}{k_1k_2k_3}\right][\mathrm{C_2H_4}] + \frac{k_{-1}}{k_1k_2}$$

Mechanism III

$$slope = \left[\frac{k_{-1}k_{-2}(k_{-3}+k_4)}{k_1k_2k_3k_4}\right][\mathrm{C_2H_4}]$$

We have obtained slopes from numerous $1/k_{obs}$ *vs.* [BA] plots and plotted these slopes *vs.* [C_2H_4]. Unfortunately, the solubility of C_2H_4 proved to vary as a function of [BA] and the simple graphical method described above did not give a solution. In collaboration with Professor James P. Kohn of the Chemical Engineering department at Notre Dame University we experimentally measured the solubility of C_2H_4 as a function of [BA] and were then able to calculate the actual [C_2H_4] for each of our kinetic experiments. Multiple regression of the kinetic data implicated **mechanism II**.

The mononuclear substitution reaction in eq 2 shows a complication that provides insight into the mechanism of this reaction. At lower concentrations of BA the *di*osmacyclobutane $Os_2(CO)_8(\mu\text{-}\eta,\eta'\text{-}H_2C{=}CHCO_2Bu)$ is observed as a coproduct from the *mono*nuclear olefin exchange reaction. No induction period is observed in the formation of this binuclear product, and the **3**/**4** ratio decreases with decreasing BA concentration. These results suggest the following mechanism of formation. The resulting rate law, written in terms of disappearance of the starting material **1**, correctly predicts the behavior of the system as [BA] is varied. The observation that significant amounts of **4** are formed at low [BA] provides compelling evidence (in addition to the saturation kinetics already noted at high [BA]) for the intermediacy of $Os(CO)_4$ in eq 2.



4 (3)

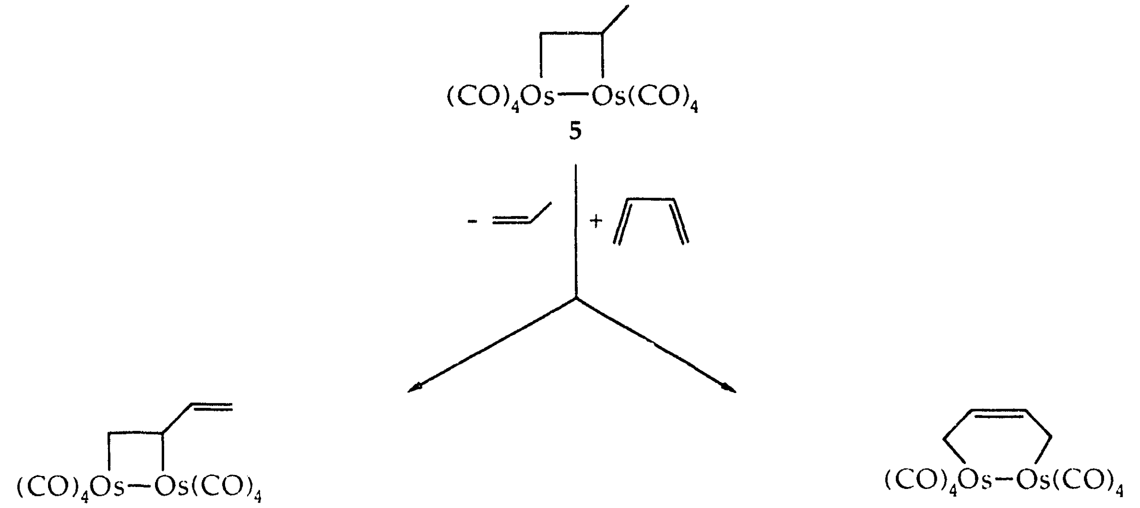
$$\boxed{-\frac{d[\mathbf{2}]}{dt} = \frac{k_5 k_6 [\mathbf{2}][BA] + k_5 k_7 [\mathbf{2}]^2}{k_{-5}[H_2C=CHCH_3] + k_6[BA] + k_7[\mathbf{2}]}}$$

D. Reaction of dienes and allenes with diosmacyclobutanes

Question to be Answered: Do dienes add 1,2 or 1,4 to $Os_2(CO)_8$?

Our conclusion in the preceding section (that **Mechanism II** is correct) implies that the exchange reactions of diosmacyclobutanes do not involve free $(CO)_4Os{=}Os(CO)_4$. However, before that result had been established we decided to investigate whether these reactions gave 1,4 or 1,2 addition products when the $(CO)_4Os{=}Os(CO)_4$ unit was transferred to a diene. The former (1,4 addition) is of course observed when a carbon-carbon double bond reacts with a diene, and would be expected with free $(CO)_4Os{=}Os(CO)_4$ (Scheme I).

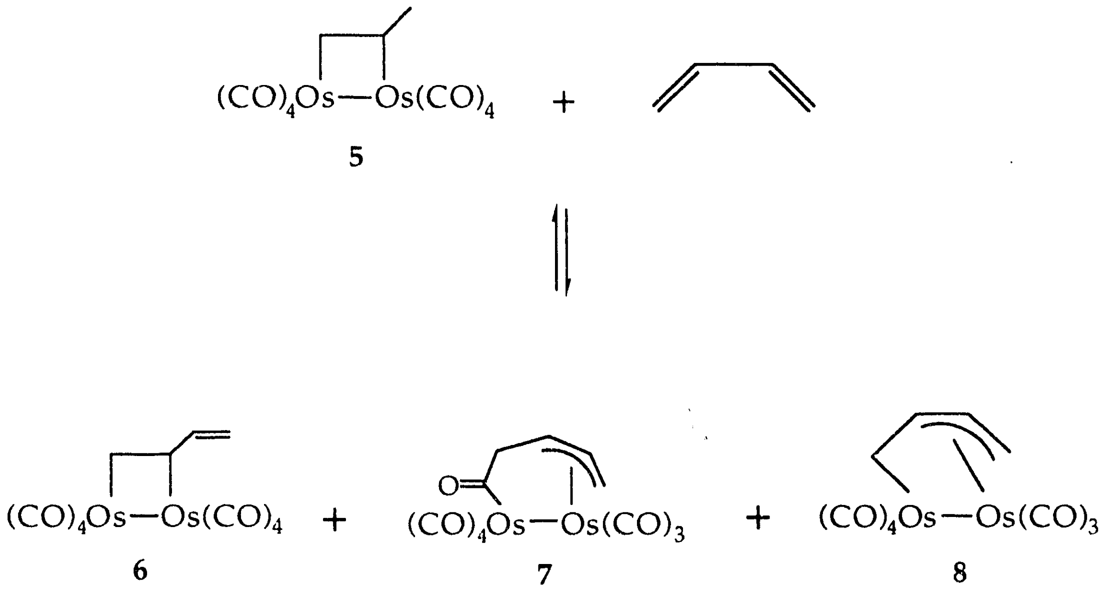
Scheme I



(1, 2-addition product)

(1, 4-addition product)

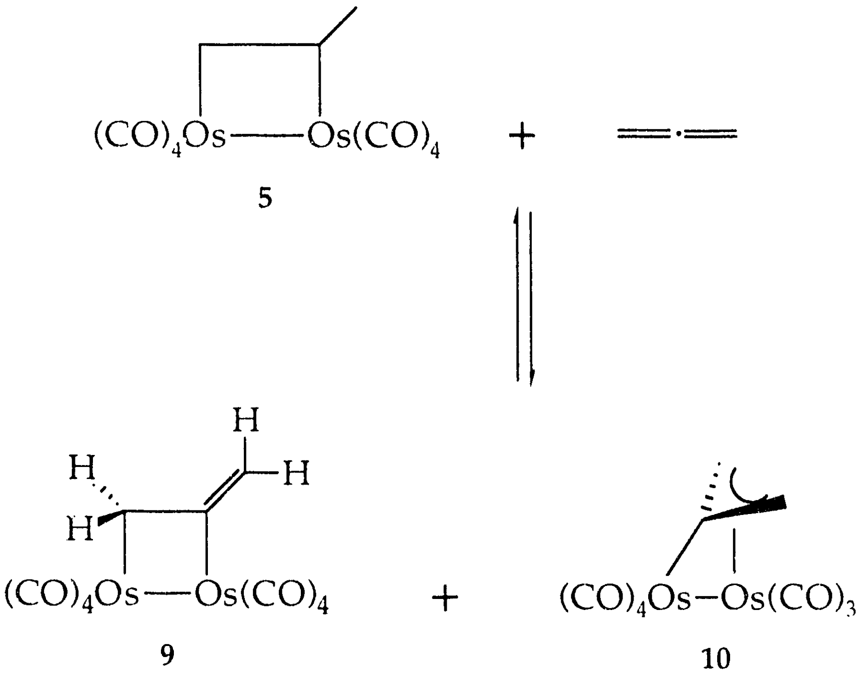
Instead, the reaction between the diosmacyclobutane **5** and butadiene (eq 4) gave the 1,2 addition product **6** along with compounds **7** and **8**. The kinetic product **6** rearranges to **7**.



(4)

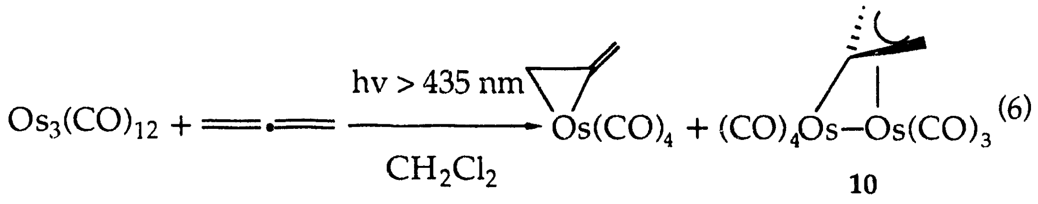
Compound **8** is also obtained from the reaction of $[Os_2(CO)_8]^{2-}$ with either *cis-* or *trans*-$ClCH_2CH{=}CHCH_2Cl$ or with $CH_2{=}CHCHClCH_2Cl$. Photolysis of $Os_3(CO)_{12}$ in the presence of butadiene gives the dinuclear compounds **7** and **8** as well as $Os(CO)_3$(butadiene).

The transfer of the $(CO)_4Os{=}Os(CO)_4$ unit to an allene also occurs by 1,2 addition (eq 5).



(5)

The kinetic product **9** rearranges to the more thermodynamically stable and previously reported[12] **10**. (The 1,2 addition product **9** represents a new bonding mode for allene as a bridging ligand in dinuclear centers.[13]) Photolysis of $Os_3(CO)_{12}$ in the presence of allene gives $Os(CO)_4$(allene) and **10** (eq 6).



The observation of 1,2 addition products in both of the above cases is consistent with, and indeed predicted by, the mechanism established in Section C.

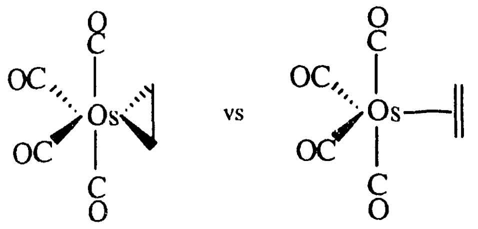
E. "The Structure of $Os(CO)_4(C_2H_4)$, an Osmacyclopropane", B.R. Bender, J.R. Norton*, M.M. Miller, O.P. Anderson, and A.K. Rappé*, *Organometallics* 1992, *11*, 3427-3434.

A nearly complete draft of another publication — describing the structure of $Os(CO)_4(C_2H_4)$ in a nematic phase solvent — was written almost a year ago. It lacks only the appropriate vibrational corrections, which require the normal mode data that our collaborators at East Anglia (Anson and Sheppard) have promised but not yet delivered.

Question to be Answered: how much osmacyclopropane character does $Os(CO)_4(C_2H_4)$ possess? **Goal:** synthesis of coordinatively unsaturated alkyl carbonyl cations

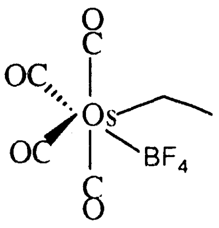
The value of $^1J_{^{13}C-^{13}C}$ for an ethylene coordinated to $Os(CO)_4$ has been determined from the ^1H NMR spectrum of $Os(CO)_4(\eta^2\text{-}^{13}C_2H_4)$. X-ray analysis shows the geometry of $Os(CO)_4(\eta^2\text{-}C_2H_4)$(**11**) to be approximately trigonal bipyramidal, with the ethylene carbons twisted out of the equatorial plane by 4.0°. The axial carbonyls of **11** tilt *toward* the coordinated ethylene, with a C1–Os–C1' angle of 171.3(5)°. The optimal geometries of $Os(CO)_4$, $H_2Os(CO)_4$, and **11** have been calculated by Hartree Fock methods. The orbital amplitude contour diagrams of a GVB(6/12) wavefunction for **11** show that the axial bending occurs in order to mix in virtual p_π character and improve backbonding to the equatorial carbonyls; they also show that **11** is best described as a metallacyclopropane.

One would thus expect the *kinetic* site of electrophilic attack on **11** to be carbon, despite the strength of the Os-H bond. We have therefore begun to examine the protonation of **11** by acids with weakly coordinating anions. (The potential uses of the cations thereby generated will be discussed in "Plans for Future Research".)



11

Use of $HBF_4 \bullet Me_2O$ in CH_2Cl_2 gives the insoluble **12** with η^1-BF_4^-; the BF_4^- is displaced by coordinating solvents such as acetone to give **13** Use of CF_3SO_3H gives the soluble **14**. We have seen no evidence for Os–H bond formation, or even for an agostic interaction between the Os and a C–H bond.



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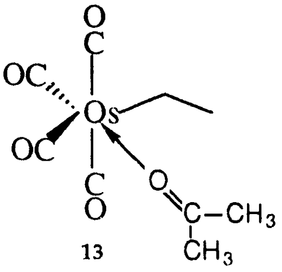
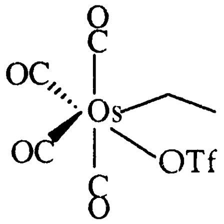


13



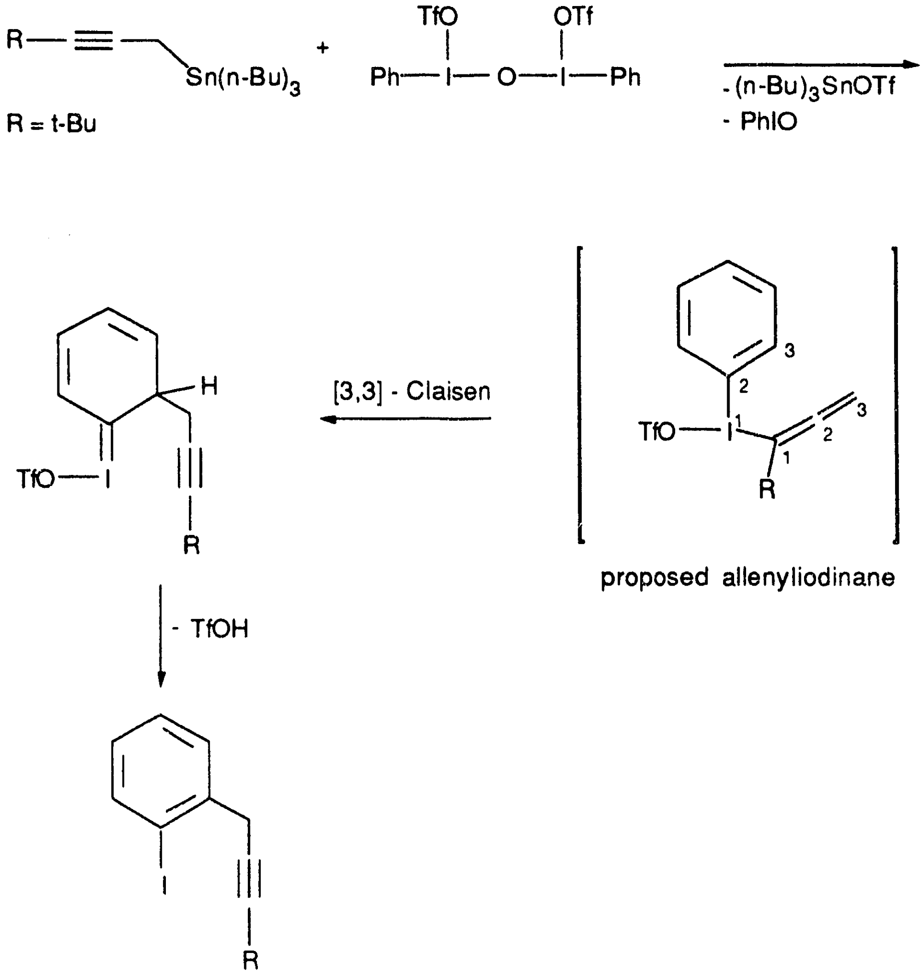
14

Like $CpRe(CO)_2$(alkene) complexes,[14] $Os(CO)_4$ complexes of substituted olefins give cationic allyl complexes when treated with Ph_3C^+. For example, $Os(CO)_4(CH_3CH{=}CH_2)$ gives $[Os(CO)_4(CH_2CHCH_2)]^+$, and $Os(CO)_4(CH_3CH_2CH{=}CH_2)$ gives $[Os(CO)_4(CH_3CHCHCH_2)]^+$.

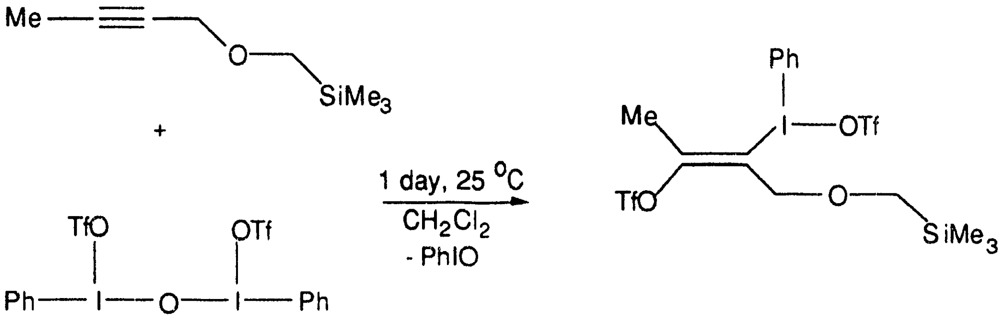
F. "Reaction of μ-Oxobis[(trifluoromethanesulfanato)(phenyl)iodine(III)] with Group 14 Propargyl Derivatives and a Propargyl Ether", D.A. Gately, T.A. Luther, J.R. Norton*, M.M. Miller, and O.P. Anderson, *J. Org. Chem.* 1992, 57, 6496-6502.

Question to be Answered: does $[PhI(OTf)]_2O$ react with alkynes in any useful way? (We used the reaction of this reagent with olefins to generate the vicinal ditriflates required for the synthesis of diosmacyclobutanes.)

We have discovered a novel allenyl "Claisen" rearrangement while exploring the reactions of an I(III) reagent with triple bonds.[15] We have shown that the intramolecular H/D isotope effect is negligible, as previously reported[16] for the Claisen rearrangement of 2-deuteriophenyl propargyl ether.



We have discovered that a side chain ether oxygen can control the regioselectivity with which the reagent adds to triple bonds. The reaction below gives only the product shown.



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