Kinetics of Diosmacyclobutane Exchange Reactions

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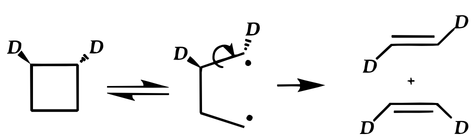
Abstract: Diosmacyclobutanes $Os_2(CO)_8$(olefin) undergo facile exchange reactions with olefins and acetylenes. An associative mechanism is excluded by the observation of saturation kinetics as the concentration of the entering olefin (butyl acrylate) is increased. Multivariate analysis of the rate as a function of [C_2H_4] (determined from solubility measurements in decane/butyl acrylate mixtures) and [butyl acrylate] suggests a stepwise mechanism in which the departing olefin migrates to a terminal position and then undergoes associative exchange with the entering olefin. The straightforward dissociative exchange of the olefin ligands in $Os(CO)_4$(olefin) shows saturation at much lower concentrations of entering olefin.

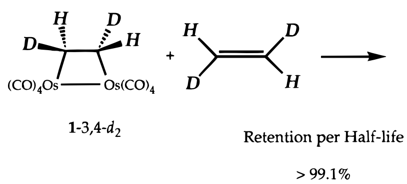
Introduction

Metallacycles are involved in many important reactions in solution[1] and have been proposed as models for the chemisorption of organic species on the surface of heterogeneous catalysts.[2] Some time ago we reported that the exchange reactions of (μ-1,2-ethanediyl)octacarbonyldiosmium (**1**) proceed with retention of stereochemistry[3] —a finding inconsistent with the intermediacy of a diradical like that involved in the fragmentation of the isolobal[4] cyclobutane, eq 1.[5]



(1)

Greater than 99.1% retention of stereochemistry per half-life was observed when the exchange of free *trans*-ethylene-1,2-d_2 with *trans*-**1**-3,4-d_2 was followed for 66 half-lives, eq 2.[6]

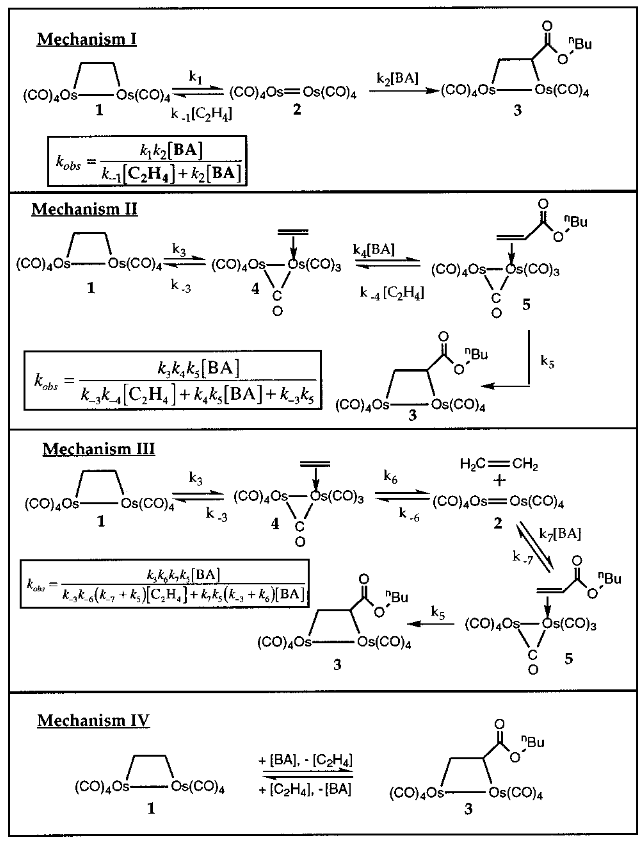


(2)

The simplest mechanism that can be proposed is the [$_\pi 2_s$ + $_\pi 2_s$] cycloreversion shown as mechanism I in Scheme 1. After fragmentation of **1** to free ethylene and octacarbonyldiosmium, **2**, a [$_\pi 2_s$ + $_\pi 2_s$] cycloaddition of the incoming unsaturated molecule (butyl acrylate (BA) in Scheme 1) to **2** would form the substituted diosmacyclobutane **3**. Such apparent [$_\pi 2_s$ + $_\pi 2_s$] cycloadditions are ubiquitous in organometallic chemistry.

Compound **2** has been observed in an argon matrix after photolysis of $Os_2(CO)_9$ or **1** (eq 3),[7] and in solution (eq 4)[8] and

Scheme 1. Possible Mechanisms for Diosmacyclobutane Exchange Reactions



$$k_{obs} = \frac{k_1k_2[\mathbf{BA}]}{k_{-1}[\mathbf{C_2H_4}] + k_2[\mathbf{BA}]}$$

$$k_{obs} = \frac{k_3k_4k_5[\mathrm{BA}]}{k_{-3}k_{-4}[\mathrm{C_2H_4}] + k_4k_5[\mathrm{BA}] + k_{-3}k_5}$$

$$k_{obs} = \frac{k_3k_6k_7k_5[\mathrm{BA}]}{k_{-3}k_{-6}(k_{-7}+k_5)[\mathrm{C_2H_4}] + k_7k_5(k_{-3}+k_6)[\mathrm{BA}]}$$

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

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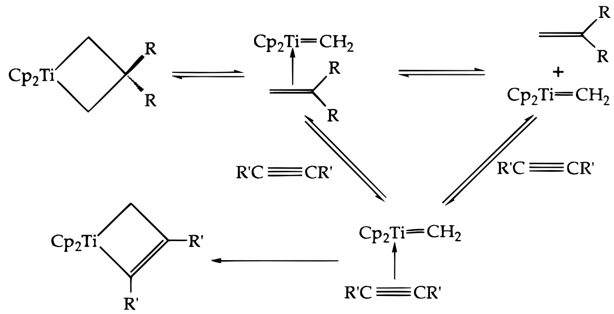
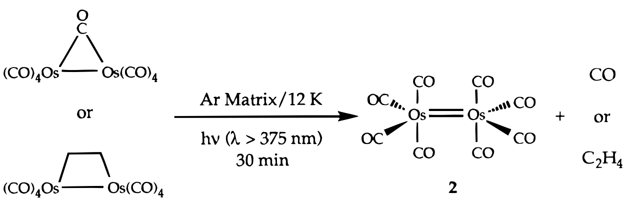
Scheme 2. Exchange of Titanocyclobutanes with Alkynes via Carbene−Alkene Intermediates



in the gas phase (eq 5) after flash photolysis.[9] However, it should be stressed that formation of **2** from **1** in eqs 3 and eq 4 is a photochemical process, not the proposed thermal process of mechanism I. The thermal [$_\pi 2_s + _\pi 2_s$] cycloaddition and cycloreversion in mechanism I is analogous to those disallowed[10] in all-carbon systems.



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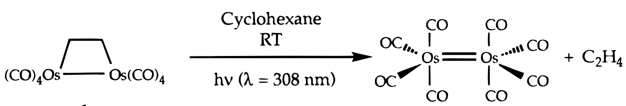
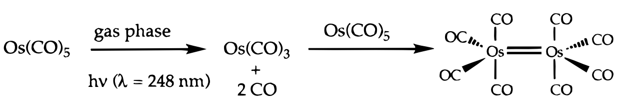


1 2 (4)



2 (5)

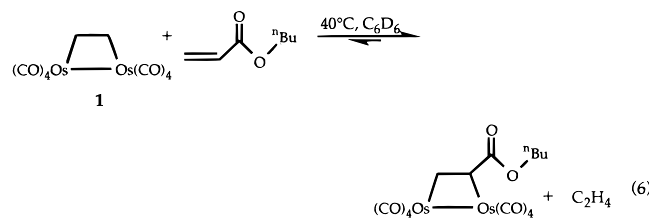
Three other mechanisms merit consideration. All are analogous to those offered by Grubbs and co-workers for the reaction of titanacyclobutanes with alkenes and alkynes.[11] Mechanisms II and III in Scheme 1, involving associative and dissociative exchange with an intermediate, derive from the titanacyclobutane mechanisms shown in Scheme 2. The associative mechanism IV in Scheme 1 derives from an analogous titanacyclobutane mechanism.

The carbene−alkene intermediate in Scheme 2 is related by the isolobal analogy (Cp_2Ti to CH_2 to $Os(CO)_4$)[4] to the ring-opened intermediate **4** in mechanisms II and III in Scheme 1. The dinuclear **4** is known as a matrix species[7] and has been identified as a transient in solution,[8] returning to **1** with a rate constant of 8 s^{-1} at 25 °C. Mechanisms II and III both begin with slippage of the ethylene bridge onto a single osmium, forming **4**. In II the ethylene ligand of **4** is associatively exchanged for incoming BA, forming **5** and then **3**; in III the ethylene ligand of **4** dissociates, and the resulting **2** reacts with BA to give **5** and then **3**.

Anslyn and Grubbs examined the product ratios when $Cp_2Ti(CH_2)$ from different titanacyclobutanes was trapped by the same alkene/alkyne mixtures, and argued for associative exchange with the carbene−alkene intermediate.[11a] Subsequently Hawkins and Grubbs examined the geometry of asymmetrically substituted α-methylenetitanacyclobutanes exocyclic double bond during substitution reactions and concluded that the carbene−ethylene intermediate either underwent dissociative exchange or exchanged rapidly with free ethylene.[11c] The present paper describes a series of experiments and a detailed kinetic study that rule out three of the mechanisms in Scheme 1 and implicate mechanism II, associative exchange with the coordinated olefin in the intermediate. These results, along with those of Grubbs and co-workers cited above, suggest a common mechanism for all metallacyclobutane formation and fragmentation reactions.

Results

Reaction of $Os_2(CO)_8(C_2H_4)$ with Alkenes and Alkynes. The parent diosmacyclobutane **1** is available along with $Os(CO)_4(C_2H_4)$ in good yield via the photolysis of $Os_3(CO)_{12}$ with ethylene.[12,13] Several diosmacyclobutanes and diosmacyclobutenes can be prepared by similar photochemical reactions.[12b−d] However, the thermal exchange reactions of diosmacyclobutanes with alkenes, alkynes, and even carbon monoxide have proven more generally useful (see Table 1 and eq 6).[3,7,12b−e,14]



1 3 (6)

Alkenes with electron-withdrawing substituents, and alkynes, are incorporated into these metallacycles in preference to alkenes with electron-donating substituents. The most useful starting material is the diosmacyclobutane **1**, because it can be prepared in relatively high yield and is reasonably stable, yet reactive enough that moderate temperatures (∼40 °C) lead to convenient exchange rates. The propene analog, $Os_2(CO)_8$(propene), is less useful, with its lower stability resulting in substantial losses when it is purified.

The synthesis of $Os_2(CO)_9$ (eq 7)[7] shows how these equilibria can be exploited synthetically: the pressure bottle in which the reaction is conducted is repeatedly vented, thus removing propene from the system and pushing a thermodynamically

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(13) The yields of $Os(CO)_4(C_2H_4)$ and **1** are about 30% and 65% (by weight) from $Os_3(CO)_{12}$.

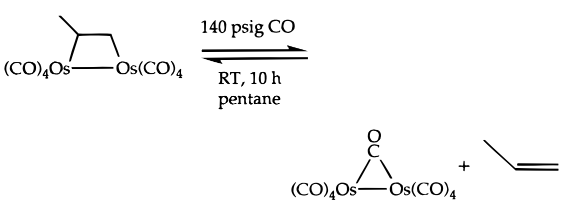
(14) (a) Hembre, R. T. Ph.D. Thesis, Colorado State University, Fall 1987. (b) Bender, B. R. Ph.D. Thesis, Colorado State University, Summer 1990. (c) Scott, C. P. Ph.D. Thesis, Colorado State University, Summer 1988.

Table 1. Exchange Reactions of $Os_2(CO)_8$(alkene)

alkene	incoming olefin or acetylene	solvent/temperature (°C)	yield (%)	ref
C_2H_4	BA[a]	decane/40	see exptl	this work
C_2H_4	BA[a]	C_6D_6/40	92	this work
C_2H_4	MP[b]	C_6D_6/47.5	83	this work
C_2H_4	DMM[c]	C_6D_6/42.5	71	this work
C_2H_4	DTBAD[d]	C_6D_6/35	77	this work
C_2H_4	DMAD[e]	C_6D_6/40	< 44	this work
C_2H_4	NMMI[f]	C_6D_6/42.5	–	this work
C_2H_4	DMFum[g]	C_6D_6/40	91	this work
C_2H_4	NTBMI[h]	C_6D_6/40	80	this work
C_2H_4	DIBFum[i]	C_6D_6/40	70	this work
C_2H_4	MA[j]	benzene/35	80	14c
C_2H_4	AC[k]	benzene/35	85	14c
C_2H_4	MP[b]	benzene/35	77	14c
MA[j]	DMAD[e]	toluene/80	47	12b
C_2H_4	DMAD[e]	pentane 25–35	50	12c,e
MA[j]	DPA[l]	toluene/82	3	12 b
C_2H_4	DPA[l]	toluene/74	20	12b,e
MA[j]	HFB[m]	toluene/68–75	20	12b
C_2H_4	HFB[m]	pentane/25–35	5 - 20	12c
MA[j]	DMM[c]	hexanes/64	65	12b
C_2H_4	3-B,2-O[n]	pentane/25–35	86	12c,e
C_2H_4	MP[b]	pentane/25–35	70	12c,e
MA[j]	MAH[o]	toluene/80	54	12b
C_2H_4	DEM[p]	not reported	“good”	12c
C_2H_4	DIPD[q]	not reported	35	12c
C_2H_4	*T*BL[r]	not reported	–	12c

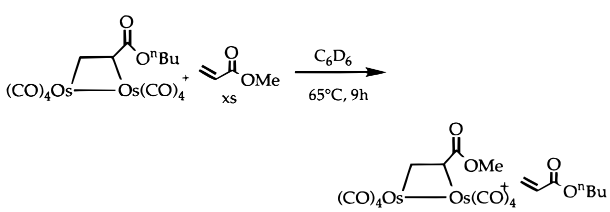
[a] Butyl acrylate. [b] Methyl propiolate. [c] Dimethyl maleate. [d] Di-*tert*-butyl acetylenedicarboxylate. [e] Dimethyl acetylenedicarboxylate. [f] *N*-Methylmaleimide. [g] Dimethyl fumarate. [h] *N-tert*-Butylmaleimide. [i] Diisobutyl fumarate. [j] Methyl acrylate. [k] Acrolein. [l] Diphenylacetylene. [m] Hexafluoro-2-butyne. [n] 3-Butyn-2-one. [o] Maleic anhydride. [p] Diethyl muconate. [q] Diisopropyldiazadiene. [r] *trans*-benzal acetone.

unfavorable reaction to completion. More typical are thermodynamically favorable displacements like the one in eq 6.



(7)

Even very stable diosmacyclobutanes undergo exchange, although under more severe conditions than **1** requires. When $Os_2(CO)_8$(BA) was heated with a large excess (>10 equiv) of methyl acrylate (MA) in C_6D_6 solution, the coordinated BA was replaced by MA over the course of 9 h (eq 8). With a large excess of BA it was possible to carry out the same reaction in the reverse direction (eq 9).



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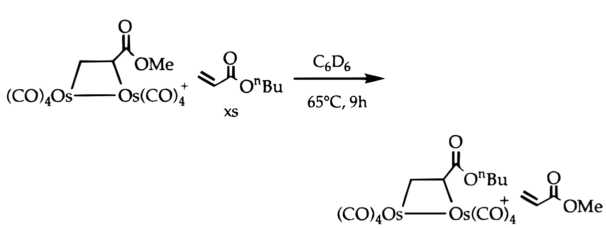
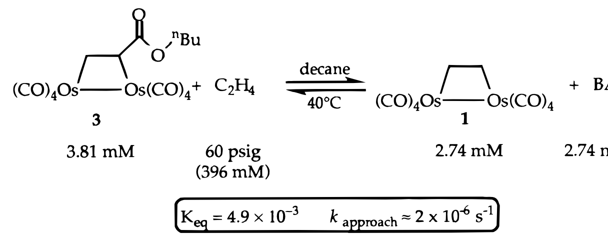


(9)

The equilibrium constant for eq 10 (the reverse of eq 6, carried out in decane) was measured by heating a decane solution of **3** (6.55 mM) to 40 °C and monitoring the approach to equilibrium. At equilibrium each species had the concentration shown, implying an equilibrium constant of 4.9×10^{-3}.

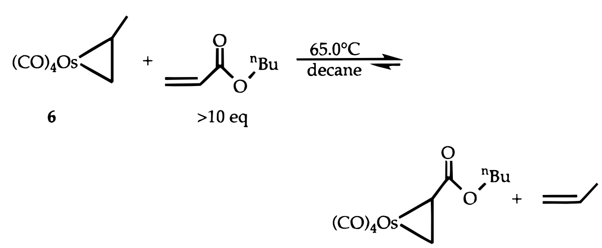


(10)

All the new alkene exchange reactions reported in Table 1 proceed cleanly and quantitatively, although difficulties in separating some products from excess alkene result in lower isolated yields. Exchange reactions with alkynes are generally more complex; small amounts of metallic coproducts are observed, and in some cases (e.g., diphenylacetylene) large amounts of trimerized alkyne.

Kinetics of Reaction 6 as a Function of [BA]. The rate of reaction 6 should increase linearly with [BA] if mechanism IV is operative, while it should exhibit saturation behavior if any of mechanisms I–III is correct. In preliminary experiments under N_2 we measured the rate of reaction 6 in decane as a function of [BA], with no ethylene present other than that formed as a product of the reaction. The results are shown in Table 2 and plotted in part a of Figure 1. The rate does *not* increase linearly with [BA].

Kinetics of the Reaction of $Os(CO)_4$(propene) (6) with BA as a Function of [BA]. Curiosity about the high concentrations of BA required to achieve saturation in Figure 1a led us to examine the analogous mononuclear reaction (eq 11). Huber and Poë have established a dissociative mechanism for reaction 12,[15] and Cardaci has established a dissociative mechanism for $Fe(CO)_4$(alkene) with a variety of incoming ligands.[16]



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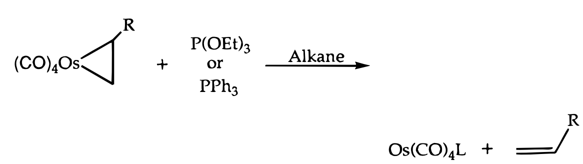


(12)

In preliminary experiments under N_2 we measured the rate of reaction 11 as a function of [BA], with no ethylene present other than that formed as a product of the reaction. Part b of Figure 1 and Table 2 show that k_{obs} for reaction 11 approaches a value of $3.85(11) \times 10^{-4}$ s^{-1} as [BA] is increased. This result is consistent with the presumption that reaction 11, like reaction 12, occurs by a dissociative mechanism.

Combined Effect of [C_2H_4] and [BA] on Reaction 6. The rate equations for mechanisms I–III in Scheme 1 are written

(15) Huber, B. J.; Poë, A. J. *Inorg. Chim. Acta* **1994**, *227*, 215–221.
(16) (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.

Table 2. Observed Rate Constants for the Reaction of Ethylene Osmium Complexes with Butyl Acrylate in the Absence of Added Ethylene[a]

ethylene complex	[BA] (M)	$10^5 \times k_{obs}$ (s^{-1})
	$T = 40$ °C	
1	0.221	6.00 (9)
1	0.439	6.38 (7)
1	2.38	10.2 (2)
1	4.65	13.2 (3)
1	6.98	15.2 (5)
	$T = 65$ °C	
6	1.02	29.1 (10)
6	2.00	36.2 (16)
6	6.23	38.5 (11)

[a] In decane, with concentrations of **1** or **6** about 8 mM.

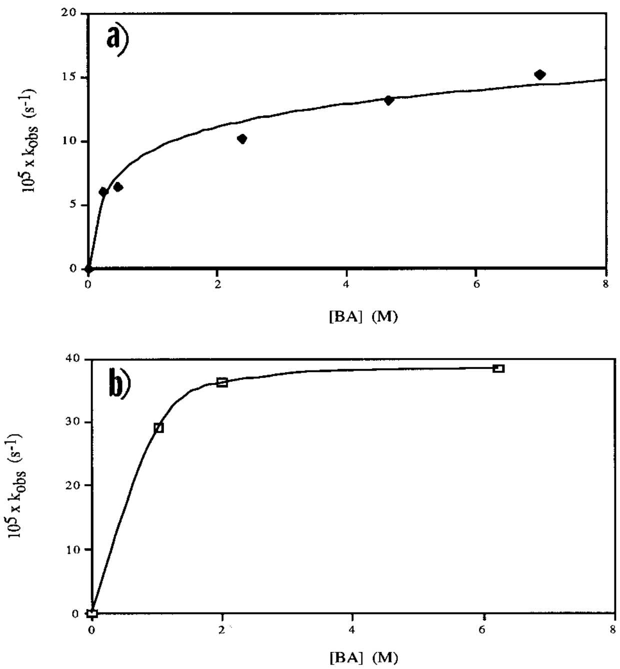


Figure 1. Dependence of k_{obs} on [BA] in the reactions of (a) $Os_2(CO)_8C_2H_4$, **1** (40 °C, decane, [**1**] = 8.25 mM) and (b) $Os(CO)_4$(propene), **6** (35 °C, decane, [**6**] = 15 mM).

Table 3. Pseudo-First-Order Rate Laws for Mechanisms I−III Written in Double Reciprocal Form

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

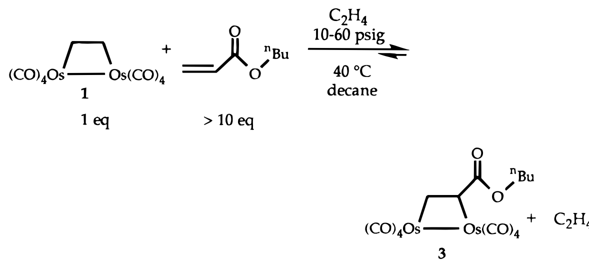
$$\frac{1}{k_{obs}} = \left[\frac{k_{-3}k_{-4}}{k_3k_4k_5}[C_2H_4] + \frac{k_{-3}}{k_3k_4}\right]\frac{1}{[BA]} + \frac{1}{k_3}$$

Mechanism III

$$\frac{1}{k_{obs}} = \left[\frac{k_{-3}k_{-6}(k_{-7}+k_5)}{k_3k_6k_7k_5}[C_2H_4]\right]\frac{1}{[BA]} + \frac{k_{-3}+k_6}{k_3k_6}$$

in reciprocal form in Table 3. In all three cases k_{obs} is a function of $[C_2H_4]$ and 1/[BA], because C_2H_4 and BA compete for the intermediates in each mechanism. At constant $[C_2H_4]$ a double reciprocal plot (k_{obs}^{-1} vs $[BA]^{-1}$) will yield a straight line if any of these mechanisms is correct. The intercept of such a plot will be equal to $1/k_1$ for mechanism I, $1/k_3$ for mechanism II, and $(k_{-3} + k_6)/(k_3k_6)$ for mechanism III. Its slope will be equal to the factors within the brackets in Table 3. Comparing them reveals a difference that can be exploited: only the slope factor for mechanism II is a *two*-term expression.

We therefore examined the rate of reaction 6 as a function of [BA] at various $[C_2H_4]$. We carried out these experiments in decane (eq 13) in order to ensure that the vapor over the solution contained only C_2H_4. The results of those experiments are given in Table 4.



(13)

We then considered the possibility that, at constant C_2H_4 gauge pressure, $[C_2H_4]$ varied significantly with the percentage of butyl acrylate in the solution. Indeed, as shown in Figure 2, the experimentally determined[17] $[C_2H_4]$ did depend on %BA for the relevant ethylene gauge pressures.

The ethylene concentrations during the experiments in Table 4 were therefore calculated as a function of solution composition. (A sample calculation is given in Supporting Information.) The Henry's Law constants and molar volumes were determined experimentally for ethylene in pure decane and pure BA. The solution mole fraction of C_2H_4 could then be calculated for decane or BA under any relevant gauge pressure of ethylene, and the concentration of C_2H_4 in decane or BA obtained from a molar volume vs mole fraction plot (e.g., Figure A2 in Supporting Information). The concentration of ethylene for each gauge pressure in the mixed solvents in Table 4 was then determined by linear interpolation (as in Figure 2) between the concentration of C_2H_4 in decane and that in BA.

If the rate equations corresponding to mechanisms I−III are written in the form in Table 5, multivariate analysis can be used to solve for the coefficients *a*, *b*, and *c*. The coefficient *b* will be *zero* in the case of mechanisms I and III, and *nonzero* in the case of mechanism II.

Multivariate analysis was performed on the global data set using the program *MINITAB*;[18] the data points were weighted by the estimated standard deviations of the $1/k_{obs}$ values. Rejection of outliers eliminated five experiments from the data set.[19] The multivariate analysis showed that *b* is 1850 mol s/L ± a 99% confidence interval of 860 mol s/L; it gave *a* as 15540(1260) s and *c* as 8790(430) s, with the uncertainties again being 99% confidence intervals. Thus we can state that *b* is *nonzero*, a result consistent with mechanism II and inconsistent with mechanisms I and III. The largest residual, or deviation from the fit, is slightly more than 12% of the corresponding rate, and the average deviation of an experimental value from the corresponding calculated value is 5.0% (see Figure C, Supporting Information).

The values of the three coefficients yield further insight into the details of the exchange reaction. The reciprocal of the coefficient *c* gives $11.4(6) \times 10^{-5}$ s^{-1} for k_3, the rate constant for the opening of the ring of **1**. As the equation for mechanism II in Table 5 shows, k_3 should also be available from k_{obs} in the

(17) Experiments conducted at The University of Notre Dame in collaboration with Dr. James P. Kohn, Department of Chemical Engineering.

(18) MINITAB Statistical Software, 3081 Enterprise Dr., State College, PA 16801-2756.

(19) Even if the rejected experiments are included in the regression, *b* is 1020 mol s/L, ± a 99% confidence interval of 720 mol s/L.

Table 4. Observed Rate Constants for Reaction 6 (40 °C) at Various [Butyl Acrylate] and [C_2H_4]

[BA] (M)	$P_{C_2H_4}$ (psig)	[C_2H_4]^a (M)	[C_2H_4]^a/[BA]	$10^5 \times k_{obs}$ (s^{-1})^b	[BA] (M)	$P_{C_2H_4}$ (psig)	[C_2H_4]^a (M)	[C_2H_4]^a/[BA]	$10^5 \times k_{obs}$ (s^{-1})^b
0.518	10	0.117	0.227	6.37(24)	2.74	30	0.245	0.089	10.1(2)
0.347	10	0.117	0.336	5.41(10)^c	0.441	40	0.287	0.652	4.47(8)
0.209	10	0.116	0.555	4.61(14)^{c,d}	0.479	40	0.287	0.600	4.81(7)
0.254	10	0.116	0.458	4.82(17)^{c,d}	2.19	40	0.301	0.138	9.16(20)
0.505	10	0.117	0.232	6.02(9)^c	2.08	40	0.300	0.144	8.12(18)
0.505	10	0.117	0.232	6.16(7)^c	0.715	40	0.289	0.405	5.23(12)
1.02	10	0.119	0.117	7.79(13)	0.355	40	0.286	0.806	3.79(8)
2.19	20	0.183	0.083	9.23(12)	2.40	50	0.363	0.151	8.91(16)
0.287	20	0.173	0.603	4.12(8)	2.01	50	0.359	0.179	8.46(12)
0.423	20	0.174	0.411	4.71(9)	0.510	50	0.345	0.676	4.11(4)
0.506	20	0.174	0.345	5.15(8)	1.20	50	0.352	0.293	6.47(9)
0.842	20	0.176	0.209	6.27(7)	6.98	50	0.408	0.058	15.3(3)^d
6.98	20	0.206	0.030	15.2(5)^d	1.80	60	0.417	0.232	8.35(18)
0.481	30	0.230	0.479	5.13(7)	2.51	60	0.425	0.169	9.21(22)
0.336	30	0.230	0.683	4.23(11)	0.515	60	0.402	0.781	3.94(6)
1.04	30	0.234	0.225	7.05(14)	1.21	60	0.410	0.340	6.44(9)
0.410	30	0.230	0.562	4.30(4)	4.58	60	0.449	0.098	11.7(2)^e

^{a} Calculated [C_2H_4]. ^{b} k_{obs} calculated by six-peak method (see Experimental Section) except as noted. ^{c} k_{obs} calculated by four-peak method. ^{d} Eliminated from global data set by outlier rejection. ^{e} Eliminated from global data set because of a relatively high residual.

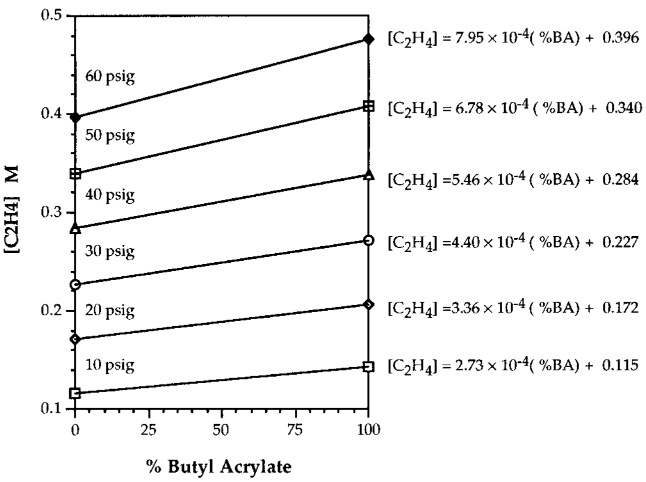


Figure 2. Plot of [C_2H_4] vs vol % BA for BA/decane mixtures at six gauge pressures of C_2H_4.

Table 5. Coefficients for Mechanisms I–III in General Equation

$$\frac{1}{k_{obs}} = a\frac{[C_2H_4]}{[BA]} + b\frac{1}{[BA]} + c$$

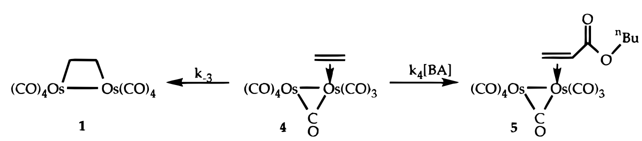
mechanism	*a*	*b*	*c*
I	$k_{-1}/(k_1k_2)$	0	$1/k_1$
II	$(k_{-3}k_{-4})/(k_3k_4k_5)$	$k_{-3}/(k_3k_4)$	$1/k_3$
III	$[k_{-3}k_{-6}(k_{-7} + k_5)]/(k_3k_6k_7k_5)$	0	$(k_{-3} + k_6)/(k_3k_6)$

limit of infinite [BA]. The fastest exchange rate measured at 40.0 °C, 15.2(5) $\times$ 10^{-5} s^{-1} (neat BA, no added C_2H_4; Table 2), is reasonably close to the estimate from the reciprocal of the regression coefficient *c*. (Solvent polarity effects may make the value of k_3 in neat BA slightly different from that in BA/decane mixtures.)

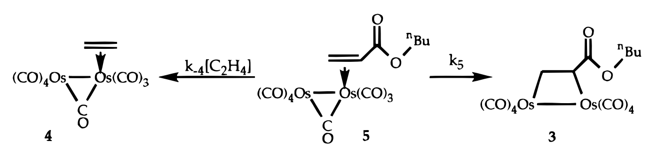
Algebraic manipulation of the equations for the coefficients *a*, *b*, and *c* corresponding to mechanism II (see Table 5) results in the ratios in eqs 14 and 15. These ratios indicate the relative ease with which the intermediates **4** and **5** undergo substitution vs rearrangement (see eqs 16 and 17). It is useful to discuss these results in terms of the alkene concentrations at which the rate of the forward reaction from **4** or **5** is equal to the rate of the reverse reaction from the same intermediate. Thus, from the ratio of the coefficients *b* and *c*, k_{-3} equals k_4[BA] at a [BA] of 0.210 M, i.e., the rate of associative replacement of C_2H_4 by BA in eq 16 is exactly equal to the rate of ethylene slippage to re-form **1**. Similarly, from the ratio of the coefficients *b* and *a*, k_5 equals k_{-4}[C_2H_4] at a [C_2H_4] of 0.199 M, i.e., the rate of associative replacement of BA by C_2H_4 in eq 17 is exactly equal to the rate of BA slippage to form **5**.

$$k_{-3}/k_4 = b/c \qquad (14)$$

$$k_5/k_{-4} = b/a \qquad (15)$$



(16)

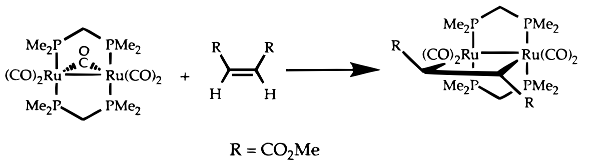


(17)

Apparently the reaction of **5** with C_2H_4 can compete effectively with ring closure (see eq 17) at relatively low ethylene concentrations (0.199 M). At slightly higher temperatures (65 °C) both the BA ligand in $Os_2(CO)_8$(BA) and the methyl acrylate (MA) ligand in $Os_2(CO)_8$(MA) exchange with free MA and BA, respectively (eqs 8 and 9). Ethylene, as a more electron rich and sterically less demanding species than MA, must be a relatively good nucleophile toward **5**. Somewhat higher concentrations (0.210 M) of BA are required for effective competition with ring closure for **4**, presumably because BA is a relatively electron poor and sterically demanding nucleophile. The very fact that inhibition is observed at low ethylene pressures is further evidence of the high nucleophilicity of ethylene.

Activation Parameters for k_3? As mentioned above, the equation for mechanism II in Table 5 suggests that k_{obs} for reaction 6 in the limit of infinite [BA] should be k_3. We therefore determined the temperature dependence of k_{obs} for reaction 6 in neat BA. A fit (weighted by the standard deviation of the individual k_{obs}'s) of the resulting data (see Table B in Supporting Information) to the Eyring equation using *MINIT-AB*[18] gave $\Delta H^{\ddagger}$ as 27.2 (4) kcal/mol) and $\Delta S^{\ddagger}$ as 10.9 (1.1) eu. However, we cannot be sure that $k_{obs} = k_3$ in neat BA at all temperatures, so there is no way of being sure that these apparent activation parameters pertain to k_3 itself. (Such results must be interpreted with care when k_{obs} is a function of more than one rate constant.[20])

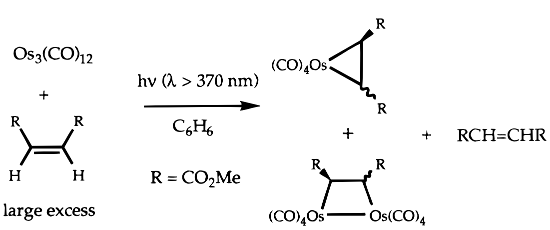
Reaction of $Os_2(CO)_8(C_2H_4)$ with Dialkyl Maleates and Fumarates. In light of our earlier observation that stereochemistry is retained in diosmacyclobutane exchange reactions involving deuterium-substituted olefins,[6] we were surprised by the report by Johnson and Gladfelter of a metallacycle formation reaction that proceeds with loss of stereochemistry, eq 18.[21] Only a dimethylfumarate adduct was obtained when dimethyl maleate was treated with $Ru_2(CO)_5(dmpm)_2$ (dmpm = bis(dimethylphosphino)methane), an analog of $Os_2(CO)_9$.



(18)

Of course the retention of stereochemistry we observed in the *trans*-$C_2H_2D_2$ experiments only argued against a diradical mechanism;[6] other mechanisms leading to loss of stereochemistry are conceivable with electron-withdrawing substituents. We have therefore looked for loss of stereochemistry in the exchange reactions of **1** with dimethyl fumarate (DMFum) and dimethyl maleate (DMM). Only a single product was obtained from DMFum, while a single—different!—product was obtained from DMM. The only other compounds present in the reaction solutions were free ethylene, excess fumarate or maleate, traces of unreacted **1**, and traces of $Os_3(CO)_{12}$ from decomposition. The product of the DMFum reaction was insoluble in benzene-d_6 and in pentane, while the product of the DMM reaction was soluble in both solvents.

Takats and co-workers have crystallographically characterized $Os_2(CO)_8(DMM)$ and $Os_2(CO)_8(DMFum)$, both prepared by the *photochemical* reaction of dimethyl maleate with $Os_3(CO)_{12}$ (eq 19).[12b,c] (Irradiation presumably isomerized some DMM to DMFum.) Significantly, they report that both the dinuclear DMFum complex and an analogous dinuclear diethyl fumarate complex are insoluble in hydrocarbon solvents, while the dinuclear DMM complex is soluble. Thus the single product of our **1** + DMFum reaction can be identified as $Os_2(CO)_8$(DMFum), leaving the single product of our **1** + DMM reaction to be $Os_2(CO)_8$(DMM).

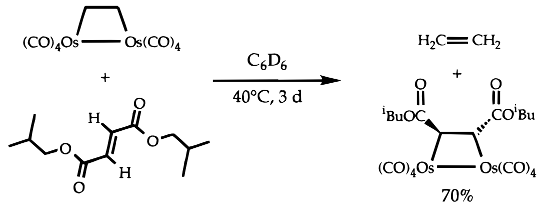


(19)

An additional diosmacyclobutane, soluble in pentane and benzene, has been prepared by treating **1** with diisobutyl fumarate (DIBF) (eq 20). The carbonyl region IR spectra of $Os_2(CO)_8$(DMFum) and $Os_2(CO)_8$(DIBF) in CH_2Cl_2 solution (see Figure D, Supporting Information) are nearly identical, but that of $Os_2(CO)_8$(DMM) is noticeably different.

(20) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw Hill: New York, 1981; pp 121−123.

(21) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1991**, *10*, 376−378.

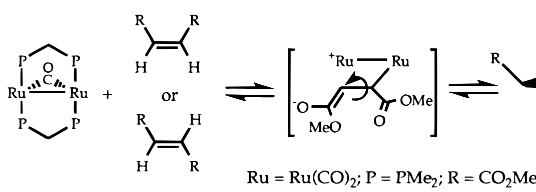


(20)

Thus, the reaction of **1** with all three incoming alkenes—DMM, DMFum, and DIBF—proceeds with retention of configuration about the double bond.

Discussion

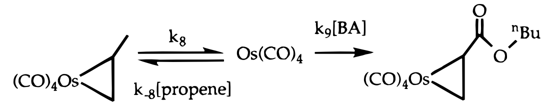
Johnson and Gladfelter have proposed two explanations for the formation of the dimethyl fumarate adduct from dimethyl maleate and $Ru_2(CO)_5(dmpm)_2$ (eq 18).[21] One suggestion was a zwitterionic intermediate, like that shown in eq 21; the other suggestion involved initial electron transfer from the pentacarbonyl Ru_2 complex to the olefin, forming a radical cationic metal complex and a radical anionic olefin. In either case rotation around the reduced C−C bond would lead to the more thermodynamically stable trans adduct. (A referee of the present manuscript has suggested an enolization mechanism.) Our results with dialkyl maleates and fumarates, in which no isomerization has been observed, show the absence of a similar mechanism in our system. (It is hard to see how rotation about the C2−C3 bond could be slower in the $Os_2(CO)_8$ system, as the dmpm ligands should make the Ru_2 framework more sterically demanding.) The transfer of charge that occurs in eq 21 (or the alternative electron-transfer mechanism) is probably feasible only when an electron-donating ligand like dmpm is present.



(21)

The evidence strongly suggests that the stereospecific exchanges in the $Os_2(CO)_8$ system arise from mechanisms like mechanism II. For reaction 6 the observed saturation behavior excludes an associative mechanism like mechanism IV, and the regression analysis of the BA/C_2H_4 competition experiments favors mechanism II over mechanisms I and III.

An additional argument for rejecting mechanisms I and III is suggested by the behavior of k_{obs} for the dinuclear reaction 6 as a function of [BA] (Figure 1a and Table 2). Figure 1b, for the analogous mononuclear reaction 11, illustrates the type of saturation behavior to be expected from a classic dissociative mechanism like that in eq 22. BA is more reactive than propene toward $Os(CO)_4$, and the only propene present is that which has dissociated. Thus k_9[BA] becomes $\gg k_{-8}$[propene] at relatively modest concentrations (about 2M) of added BA; under those conditions k_{obs} approaches k_8 and saturation is observed.



6

(22)

We should see the same behavior for *any* classic *dissociative* mechanism, including mechanism I for the dinuclear system.

Intermolecular competition between the entering and leaving olefins[22] guarantees that at relatively low concentrations of the incoming trap (BA) k_2[BA] $\gg$ $k_{-1}[C_2H_4]$ and k_{obs} will approach k_1 as a limit. Even in a more complex dissociative mechanism like mechanism III, BA and ethylene still compete for $Os_2(CO)_8$ (**2**); again, at relatively low concentrations of the incoming trap (BA), k_7[BA] will become $\gg$ $k_{-6}[C_2H_4]$, k_{obs} should approach the limiting rate of the rate of formation of **2**, and saturation should occur. Of course the preliminary experiments in Figures 1a (dinuclear) and 1b (mononuclear) were done at different temperatures, so some variation in k_{obs} could be due to differing rates of ethylene loss from the solution. However, it is difficult to imagine how saturation could require such high BA concentrations in Figure 1a if reaction 6 occurred by mechanism I or III.

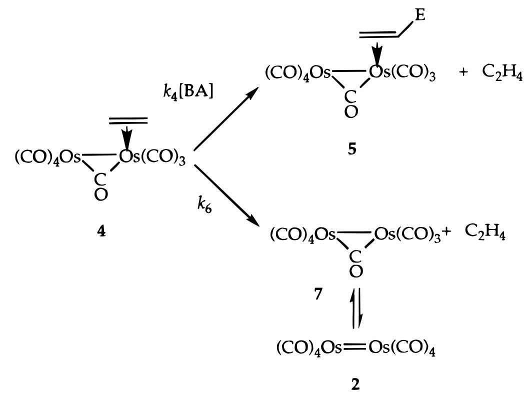
In contrast, in mechanism II attack by BA on the ring-opened intermediate **4** (rate constant k_4) competes with an *intramolecular* reaction, the reclosure of the diosmacyclobutane ring (rate constant k_{-3}). It is not clear that the reaction of BA with **4**, rate constant k_4[BA], can ever overwhelm *intramolecular* ring closure, rate constant k_{-3}. Indeed, as mentioned above, even in neat BA k_{obs} for reaction 6 may not be equal to k_3.

Associative substitution on **4** is plausible. Poë has suggested that "Associative reactions of clusters may generally be allowed because of their ability to adjust to the approach of a nucleophile by breaking one of their metal−metal bonds, so avoiding an excessive electron count".[23] Associative paths have been established for phosphorus donor substitution on trinuclear clusters such as $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Os_3(CO)_{11}(PBu_3)$,[24] and on tetranuclear clusters such as $M_4(CO)_9L_3$ (M = Rh, Ir; L_3 = $(CO)_3$, $HC(PPh_2)_3$).[25] The bridging carbonyl in **4** may contribute to its lability.[25,26]

Although mechanism II, eq 16, and Scheme 3 show BA attacking the osmium of **4** from which the ethylene is departing, it is possible that the BA attacks the *remote* osmium instead. Henderson has noted[27] that "the addition of a nucleophile to a metal site...in a... cluster need not...labilise that particular site to substitution, but...may labilise another metal site".

It is possible that mechanism III competes with mechanism II when the concentration of entering olefin or acetylene is low. At low [BA], k_4[trap] in mechanism II may become slower than k_6, the rate constant in mechanism III for dissociation of ethylene from the ring-opened intermediate **4**—leading to $Os_2(CO)_8$ (**2**) instead of **5**. (Both possibilities are shown in Scheme 3.) There is no way of knowing whether a carbonyl-bridged intermediate **7** (which would be isostructural with the CO-bridged isomer of $Fe_2(CO)_8$[28]) is the initial product of ethylene

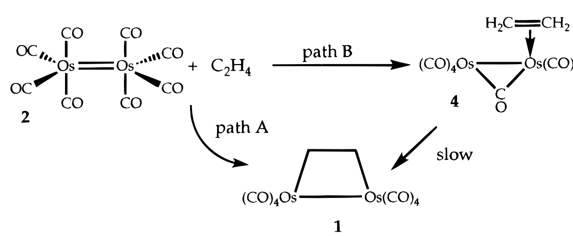
Scheme 3



dissociation from **4**, but the double-bonded species **2** has been identified by transient experiments in solution[8] and by matrix experiments.[7]

In reaction 7[7] a trace of $Os_4(CO)_{16}$[29] was observed along with the expected $Os_2(CO)_9$. In the absence of any trap, with propene swept out by N_2 gas, a solution of $Os_2(CO)_8$(propene) in decane gives the tetranuclear cluster $Os_4(CO)_{16}$.[30] It is possible that two $Os_2(CO)_8$ fragments combine directly in a variation on the k_{-6} step of mechanism III, but it is more likely that **2** associatively displaces ethylene from the ring-opened intermediate **4**, as in mechanism II.

Direct evidence that mechanism III can occur in the reverse direction can be seen when **2** is generated as a transient in solution and its reaction with ethylene is observed. Grevels and co-workers reported that **1** was re-formed in cyclohexane at room temperature by both of the two paths in eq 23.[8] Path A gave **1** directly; path B gave **4**, which slowly rearranged to **1**. Because the rate of path B was independent of $[C_2H_4]$, the



(23)

rate-determining isomerization of **2** to the carbonyl-bridged **7** was suggested as its initial step.

However, *only path B has been observed in recent experiments with methyl acrylate as the incoming olefin*.[31] The formation of an MeO_2C-substituted diosmacyclobutane proceeds entirely through a ring-opened intermediate like **4**—and thus models the k_7 and k_{-6} steps in mechanism III.

A similar result has just been reported by Casey and co-workers.[32] Incoming ligands, including ethylene and 2-butyne, attack a single rhenium in eq 24 to produce a bridged structure like **4**—implying that the formation of the dirhenacyclobutene from DMAD in eq 25 proceeds through a similar intermediate.

Additional discussion of our conclusions and their implications appears in the following manuscript.

(22) It seems safe to presume that the relative rate constants in a *hypothetical* dissociative dinuclear mechanism would be the same as in the mononuclear system, i.e., that k_7/k_{-6} in mechanism III and k_2/k_{-1} in mechanism I would be similar to k_9/k_{-8} in the mononuclear dissociative mechanism, eq 22.

(23) Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265−295.

(24) Poë, A.; Sekhar, V. C. *Inorg. Chem.* **1985**, *24*, 4376−4380 and references therein.

(25) Kennedy, J. R.; Selz, P.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1989**, *111*, 3615−3627.

(26) In some cases the introduction of bridging carbonyls is associated with an increase in lability: (a) Norton, J. R.; Collman, J. P. *Inorg. Chem.* **1973**, *12*, 476. (b) Karel, K. J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 6812. However, in other cases their introduction produces only a small rate enhancement (Poë, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209), or increases the *dissociation* rate rather than the *associative* lability (e.g., ref 3).

(27) Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1905.

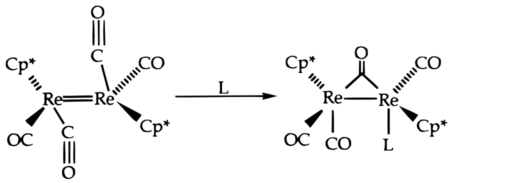
(28) (a) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 3597−3604. (b) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2403−2410.

(29) Johnson, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 8111.

(30) Spetseris, N. Ph.D. Thesis, Colorado State University, Fall 1994.

(31) Grevels, F.-W.; Klotzbücher, W. E. Personal communication.

(32) (a) Casey, C. P.; Cariño, R. S.; Sakaba, H.; Hayashi, R. K. *Organometallics* **1996**, *15*, 2640. (b) Casey, C. P.; Cariño, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617.



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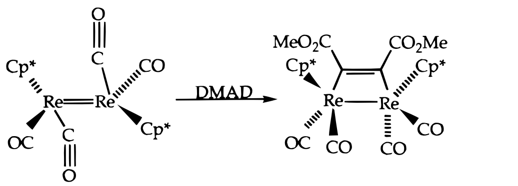


(25)

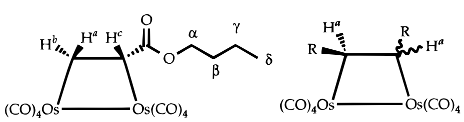
Experimental Section

General. $Os_2(CO)_8(C_2H_4)$ (**1**) was prepared from $Os_3(CO)_{12}$[33] by the method already reported.[12a,34] Decane was purified by agitation over concentrated H_2SO_4, passage through a 20 × 3 cm column of activated basic alumina, and vacuum distillation from Na/benzophenone/tetraglyme. Dimethyl acetylene dicarboxylate was distilled before use. Deuterated solvents were dried and stored over Na/benzophenone (C_6D_6) or P_4O_{10} (CD_2Cl_2) and vacuum transferred.

As purchased *n*-butyl acrylate contained 10−55 ppm hydroquinone monomethyl ester as a polymerization inhibitor. Removal of this inhibitor had no effect on the rates of reactions involving **1**, but led to significant polymerization whether or not **1** was present; therefore, all reactions were performed with *n*-butyl acrylate that still contained the inhibitor.

Infrared spectra were recorded with a Perkin Elmer PE-983 spectrometer controlled by On-Line Instrument Systems (Jefferson, GA) software on a Compaq Deskpro 386S. NMR spectra were obtained with a Bruker 270 NMR spectrometer interfaced to a Macintosh Quadra 650 running *MacNMR 4.5.8* (TecMag). Mass spectra were recorded on a Fisons VG Quattro-SQ mass spectrometer. Elemental analyses were performed by Galbraith Laboratories.

A list of abbreviations is given in Table 1. In the lists of ^{1}H NMR peaks below, side chain protons are identified by Greek letters as shown.



Reaction of $Os_2(CO)_8(C_2H_4)$ with Dimethyl Maleate (DMM). A colorless solution of **1** (18.7 mg, 0.0296 mmol) and DMM (11.1 μL, 0.0887 mmol, 3.01 equiv) in 0.5 mL C_6D_6 was prepared. The NMR tube was sealed and placed in a constant temperature bath at 42.5 °C for 139 min. The tube was then removed and allowed to cool to room temperature, and a ^{1}H NMR spectrum was recorded. A small amount of starting material was present, along with free C_2H_4 (δ 5.24 ppm), excess DMM, and two new peaks in a 3:1 ratio (δ 3.41 and 2.93, respectively) assigned to $Os_2(CO)_8$(DMM).[12b] The solution was applied to a silica gel prep TLC plate, and chromatographed with 30% CH_2Cl_2 in pentane; the isolated yield of $Os_2(CO)_8$(DMM) was 71%. Previously unreported spectroscopic data: IR (CH_2Cl_2) 2134 (w), 2092 (s), 2052 (m, sh), 2043 (vs), 2035 (s, sh), 2022 (m), 2006 (m), 1690 (w) cm^{-1}.

Reaction of $Os_2(CO)_8(C_2H_4)$ with Dimethyl Fumarate (DMFum). A colorless solution of **1** (14.4 mg, 0.0227 mmol) and DMFum (13.9 mg, 0.0964 mmol, 4.20 equiv) in 0.5 mL C_6D_6 was prepared. The NMR tube was sealed and placed in a constant temperature bath at 40.0 °C for 150 min. When the tube was removed and allowed to cool to room temperature, a white precipitate formed. Pure $Os_2(CO)_8$-(DMFum)[12b] was obtained by washing the precipitate with pentane (15.4 mg, 0.0207 mmol, 91%).

Reaction of $Os_2(CO)_8(C_2H_4)$ with Diisobutyl Fumarate (DIBF). A colorless solution of **1** (19.4 mg, 0.0306 mmol) and DIBF (35.8 μL, 0.153 mmol, 5.00 equiv) in 0.5 mL C_6D_6 was prepared. The NMR tube was sealed and kept for 3 days at 40.0 °C; its ^{1}H spectrum then showed free C_2H_4, excess DIBF, and a new compound. Four bands were observed by TLC; the first two, near the solvent front, were traces of unreacted **1** and $Os_3(CO)_{12}$, the band at $R_f \approx 0.33$ was excess DIBF, and a band at $R_f \approx 0.10$ was $Os_2(CO)_8$(DIBF). Extraction (with difficulty) by CH_2Cl_2 yielded pure $Os_2(CO)_8$(DIBF) upon recrystallization (17.9 mg, 0.0215 mmol, 70.2%). IR (pentane): 2134 (w), 2094 (m), 2051 (vs), 2034 (m), 2023 (m), 2017 (w, sh), 2005 (w), 1980 (vw), 1707 (w), 1699 (w, sh) cm^{-1}. IR (CH_2Cl_2): 2135 (w), 2094 (m), 2047 (vs), 2038 (m, sh), 2023 (m), 2007 (w), 1685 (w, br) cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.97 (dd, 2H, one of diastereotopic pair of α-CH_2), 3.72 (dd, 2H, one of diastereotopic pair of α-CH_2), 3.53 (s, 2H, H^a), 1.79 (m, $^3J_{HH}$ = 6.6 Hz, 2H, β-CH), 0.795 (d, $^3J_{HH}$ = 6.6 Hz, one of diastereotopic pair of γ-CH_3), 0.770 (d, $^3J_{HH}$ = 6.6 Hz, one of diastereotopic pair of γ-CH_3). Its mass spectrum (EI) showed P − CO at *m/e* 806 with the appropriate isotopic distribution. Anal. Calcd for $C_{20}H_{20}O_{12}Os_2$: C, 28.85; H, 2.42. Found: C, 29.20; H, 2.50.

The reaction of $Os_2(CO)_8(C_2H_4)$ with other alkenes and alkynes (except butyl acrylate) was carried out by the same procedure as the maleate and fumarate reactions above. Conditions and yields are reported in Table 1. Complete spectroscopic data are given below for new compounds; for compounds reported previously only unreported spectroscopic data are given.

$Os_2(CO)_8$(MP).[12c,14c] Small resonances attributable to a byproduct (∼5% by ^{1}H NMR) were observed in the ^{1}H NMR of the reaction mixture, but that byproduct was not isolable by the usual chromatographic techniques. IR (pentane): 2132 (vw), 2089 (m), 2044 (vs), 2035 (m), 2021 (m), 2005 (w), 1690 (vw) cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.36 (s, 1H, H^a), 3.44 (s, 3H, α-CH_3) ppm. Its mass spectrum (EI) showed a peak for the molecular ion at *m/e* 690 with the appropriate isotopic distribution. Anal. Calcd for $C_{12}H_4O_{10}Os_2$: C, 20.93; H, 0.59. Found: C, 21.19; H, <0.5.

$Os_2(CO)_8$(DTBAD). IR (pentane): 2135 (vw), 2093 (s), 2050 (vs), 2036 (m), 2023 (m), 2006 (w), 1705 (vw) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.47 (s, β-CH_3). Its mass spectrum (EI) showed a peak for the molecular ion at *m/e* 832 with the appropriate isotopic distribution.

$Os_2(CO)_8$(DMAD).[12b,d] In our hands the thermal exchange reaction gave not only the reported $Os_2(CO)_8$(DMAD) (insoluble in hydrocarbon solvents), but also a trace of $Os_2(CO)_6(DMAD)_2$,[12b,d] previously reported as a product of the photolytic reaction of $Os_3(CO)_{12}$ and DMAD. IR and ^{1}H NMR spectoscopies also showed hexamethylmellitate.[35]

$Os_2(CO)_8$(NMMI). IR (CH_2Cl_2): 2135 (w), 2094 (s), 2056 (m, sh), 2044 (vs), 2027 (m), 2013 (w, sh), 1728 (vw), 1662 (w) cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 3.11 (s, 2H, H^a), 2.97 (s, 3H, N-CH_3).

$Os_2(CO)_8$(NTBMI). IR (pentane): 2133 (vw), 2092 (m), 2041 (vs), 2028 (m), 1709 (vw), 1677 (vw), cm^{-1}. IR (CH_2Cl_2): 2134 (w). 2093 (s), 2053 (m, sh), 2043 (vs), 2026 (m), 2009 (w, sh), 1720 (vw), 1658 (w) cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 2.95 (s, 2H, H^a), 1.56 (s, 9H, N-C-(CH_3)$_3$). Its mass spectrum (EI) showed a peak for the molecular ion at *m/e* 759 with the appropriate isotopic distribution. Anal. Calcd for $C_{16}H_{11}NO_{10}Os_2$: C, 25.37; H, 1.46. Found: C, 25.07; H, 1.20.

Kinetics. Sufficient metal complex to yield an absorbance in the 0.6 to 1.0 range (in the metal carbonyl region of the IR spectrum) was dissolved in decane in a volumetric flask, the desired amount of BA was measured by weight, and the solution was diluted with decane. The solution was transferred to a Fischer & Porter pressure vessel, chilled to 0 °C to inhibit reaction, and subjected to at least 10 charge/purge cycles with ethylene (40 psig) or N_2. The vessel was then charged either with the desired pressure of C_2H_4 (measured with a calibrated C_2H_4 regulator) or with a slight positive pressure of N_2, immersed in a constant temperature bath, and magnetically stirred. Samples were withdrawn at appropriate intervals by a syringe (precooled with LN_2) through a septum, at least 3× (usually 5×) per half-life. The reaction was monitored for greater than three half-lives. Three IR scans from

(33) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859−2864.

(34) See also: (a) Poë, A. J.; Sekhar, C. V. *J. Am. Chem. Soc.* **1986**, *108*, 3673−3679. (b) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092−4093. (c) Reference 12e.

(35) (a) Diercks, R. T.; Dieck, H. *Z. Naturforsch.* **1984**, *39B*, 180−184. (b) Lindner, E.; Jansen, R.-M.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* **1989**, *8*, 2355−2360.

2100 to 1980 cm^{-1} were collected and averaged (the 4 min required for scanning proved to be insignificant for progress of the reaction at room temperature). Infinity points were taken after at least 10 half-lives; background spectra of decane/BA mixtures were subtracted.

Calculation of k_{obs}. A Macintosh program, *IR Kinetics*, took the spectra collected as a function of time, extracted absorbance data for user-determined wavelengths, and calculated k_{obs} at each wavelength of interest, along with an estimated standard deviation, *s*. The individual k_{obs}'s were then averaged to give a global rate constant (eq 26) along with its estimated standard deviation.

$$\bar{k}_{obs} = \frac{\sum_{i=1}^{i=n} k_{obs_i} w(k_{obs_i})}{\sum_{i=1}^{i=n} w(k_{obs_i})} \quad (26)$$

where

$$w(k_{obs_i}) = \frac{1}{s^2 k_{obs_i}} \quad n = \text{no. of data points}$$

In the six-peak method, three starting material peaks (2076, 2008, and 1993 cm^{-1}) and three product peaks (2085, 2046, and 1999 cm^{-1}) were followed; in the four-peak method the two peaks at 1999 and 1993 cm^{-1} were not included. Nine wavelengths centered on the maxima of each peak (±2.0 cm^{-1} at 0.5 cm^{-1} resolution) were monitored, giving 36 (four-peak method) or 54 (six-peak method) separate estimates of k_{obs}. Standard deviations of the global rate constants ranged from 0.87% to 3.83% in the C_2H_4/BA competition study, with an average of 1.88%.

Saturation Kinetics. In a typical experiment 10 mL solution of **1** (53.3 mg, 8.25 mM) and BA (3054.1 mg, 2.383 M) in decane was prepared in a Fischer & Porter pressure vessel and charged with a slight positive pressure of N_2. At 40.0 °C 18 time points were collected over 441 min. Infinity points were collected the following morning. The data was analyzed by the six-peak method, and the global rate constant was 1.015(17) × 10^{-4} s^{-1}.

Ethylene/Butyl Acrylate Competition Reactions. In a typical experiment a 10 mL solution of **1** (44.0 mg, 6.96 mM) and butyl acrylate (616.7 mg, 0.4812 M) in decane was prepared in a Fischer & Porter test tube and charged with 30 psig C_2H_4 ($[C_2H_4]_{calcd}$ = 0.23 M). At 40.0 °C 16 time points were collected over 786.4 min, and two infinity points were taken the following day; the reaction was quantitative by IR. The six-peak method gave a global k_{obs} of 5.13(7) × 10^{-5} s^{-1}.

When solutions from several kinetic experiments were combined, concentrated, and placed in a −27 °C freezer for several days, large white needles formed. Washing with cold pentane (<−50 °C) and drying *in vacuo* yielded pure **3** (92%). IR (pentane): 2129 (w), 2085 (s), 2048 (s), 2038 (vs), 2029 (s), 2015 (s), 1999 (m), 1971 (vw), 1703 (w) cm^{-1}. IR (CH_2Cl_2): 2129 (w), 2085 (s), 2038 (vs), 2029 (sh, m), 2014 (m), 1997 (w), 1680 (vw) cm^{-1}. ^1H NMR (C_6D_6): 4.07 (m, 2H, unresolved diastereotopic α-CH_2), 2.67 (dd, 1H, H^c), 2.05 (dd, 1H, H^b), 1.57 (dd, partially obscured by β-CH_2 resonances, 3H together; H^a), 1.58 (m, partially obscured by H^a resonances, together 3H, unresolved diastereotopic β-CH_2), 1.24 (m, 2H, unresolved diastereotopic γ-CH_2), 0.79 (t, 3H, $^3J_{HH}$ = 7.3 Hz, δ-CH_3). Its mass spectrum (EI) showed a peak for the molecular ion at *m/e* 734 with the appropriate isotopic distribution. Anal. Calcd for $C_{15}H_{11}O_{10}Os_2$: C, 24.62; H, 1.52. Found: C, 24.20; H, 1.27.

Measurement of Ethylene Solubility in Decane/Butyl Acrylate Mixtures.[17] Approximately 12−14 mL of solvent mixture was weighed and placed in a specially constructed high-pressure cell containing a built-in stir bar.[36] The cell was placed in a constant temperature bath

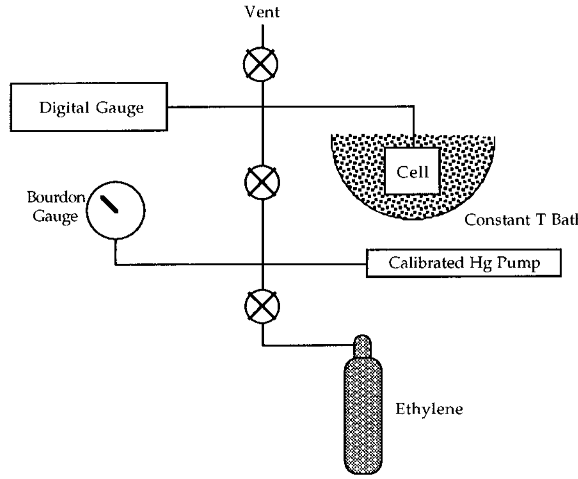


Figure 3. Apparatus for C_2H_4 solubility measurement.

equipped with a calibrated NBS platinum thermocouple and equilibrated at 40.0 °C with continous stirring. It was connected to a line of known volume (Figure 3) equipped with a digital gauge to read the pressure in the cell. A known quantity of C_2H_4 was added using a mercury pump connected to a Bourdon gauge, also of known volume. After equilibration the pressure reading and the temperatures of the cell, line, and mercury pump were recorded. The volume of liquid in the cell was read using a calibrated cathetometer. This process was repeated for 4−5 different volumes of C_2H_4, including a volume high enough to saturate the solution.

The ideal gas law with a first-order virial correction was used to calculate the total moles of C_2H_4 added to the solution at each point and at the saturation point, eq 27.

$$n_{C_2H_2} = \left(\frac{PV}{zRT}\right)_{pump} - \left(\frac{PV}{zRT}\right)_{cell+line} \quad (27)$$

$$z = 1 - \frac{BP_cP_r}{RT_cT_r}$$

The mole fraction and molar volume of C_2H_4 in the solution were calculated, and a plot of molar volume C_2H_4 vs mole fraction (Figure A2, Supporting Information) was constructed. Henry's Law constants for pure decane and pure BA were calculated by constructing a plot of pressure vs mole fraction. The slope of this plot gives the value of the Henry's Law constant. That constant varies slightly with pressure (see Figure A1 in Supporting Information); to cover the pressure range employed in the kinetics, the Henry's Law constants for pure decane (65.9) and pure BA (74.8) at 5 bar C_2H_4 were used.

Calculation of Ethylene Concentrations as Functions of Decane/Butyl Acrylate Ratio and C_2H_4 Gauge Pressure. The Henry's Law constant for the pure solvent was used along with the gauge pressure to calculate the mole fraction of C_2H_4 in solution at that pressure. The $[C_2H_4]$ at that pressure was obtained from the molar volume vs mole fraction plot (see previous section).

Plots of $[C_2H_4]$ vs the %BA were then constructed for the six different gauge pressures of C_2H_4, each containing two points corresponding to the pure solvents. The lines between each pair of points were used to complete the solubility calculations. For a given gauge pressure and a known %BA the $[C_2H_4]$ was interpolated. A sample calculation can be found in the Supporting Information.

Multivariate Regression Analysis. The data from Table 4 were imported into *MINITAB*,[18] and a weighted regression analysis was carried out. The outlier rejection procedure in *MINITAB* removed from the data set the experiments indicated. An additional experiment, at a relatively high [BA] (4.575 M), was rejected since it had a relatively large residual (−1.34 standard deviations); the remaining 29 experiments range from 0.287 to 2.736 M BA. At no point during this procedure did regression ever give a value for the coefficient *b* which included zero in its 99% confidence interval.

(36) Cell constructed by James P. Kohn, Department of Chemical Engineering, University of Notre Dame (modified version of that described in Lee, K. H.; Kohn, J. P. *J. Chem. Eng. Data* **1969**, *14*, 292).

Temperature Dependence of k_{obs} for Reaction 6. In a typical experiment a 10 mL solution of **1** (49.4 mg, 7.79 mM) in neat BA in a Fischer & Porter pressure vessel was charged with a slight positive pressure of N_2. At 45.0 °C 15 samples were collected in 148.6 min and infinity points the following day. The four-peak method gave a global k_{obs} of 31.7(6) $\times$ 10^{-5} s^{-1}.

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Supporting Information Available: Sample ethylene solubility calculation (7 pages), kinetic and spectroscopic data (3 pages), and derivation of rate laws (5 pages) (15 pages total). See any current masthead page for ordering and Internet access instructions.

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