Final Report

U. S. Department of Energy
(Grant #FG03-94ER14405)

DOE/ER/14405--T1

CATALYTIC APPLICATIONS OF MONO- AND DINUCLEAR COMPLEXES CONTAINING METAL-CARBON SIGMA BONDS

For the Period November 1, 1993 to October 31, 1996

Jack R. Norton, Principal Investigator
Colorado State University
Fort Collins, CO 80523-1872

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Final Report
Department of Energy (Grant #FG03-94ER14405)
Jack R. Norton, Principal Investigator

A. Vibrational Models for Surface Olefins and Alkylidenes.

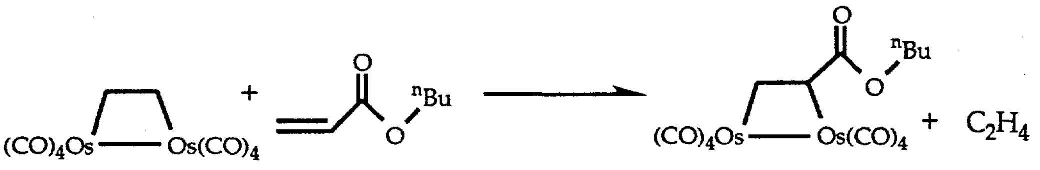
Publications: (reference 1 in this report and the following proposal.) "[(η^2-C_2H_4)$Os(CO)_4$] as a Vibrational Model for Surface Type I' Ethene Chemisorbed as a Metallacyclopropane on Metal Surfaces," C.E. Anson, N. Sheppard*, D.B. Powell, B.R. Bender and J.R. Norton, *J. Chem. Soc., Faraday Trans.*, **1994**, *90*, 1449-1454.

(ref 2) "Assignments of the Infrared and Raman Spectra of the $Os_2(\mu_2$-$CHCH_3)$ Group of [μ_2-$CHCH_3$) Os_2 $(CO)_8$] and of their **d^1** and **d^4** Isotopologues as Models for the Spectrum of such Ethylidene Groups on Metal Surfaces," C.E. Anson, N. Sheppard*, D.B. Powell, J.R. Norton*, W. Fischer, R.L. Keiter, B.F.G. Johnson, J. Lewis, A.K. Bhattacharrya, S.A.R. Knox, and M.L. Turner, *J. Am. Chem. Soc.* **1994**, *116*, 3058-3062.

B. Mechanism of the Formation and Fragmentation of Diosmacyclobutanes. A full paper has appeared that reports our work on the stereochemistry of olefin exchange into diosmacyclobutanes: (ref 3) "Retention of Stereochemistry in the Formation and Fragmentation of Diosmacyclobutanes, and Other Evidence Against a Diradical Mechanism," R.T. Hembre, D.L. Ramage, C.P. Scott and J.R. Norton*, *Organometallics* **1994**, *13*, 2995-3001. This is only the second time that *the accumulated loss of stereochemistry in a reversible reaction* has been used to quantify stereoretention.

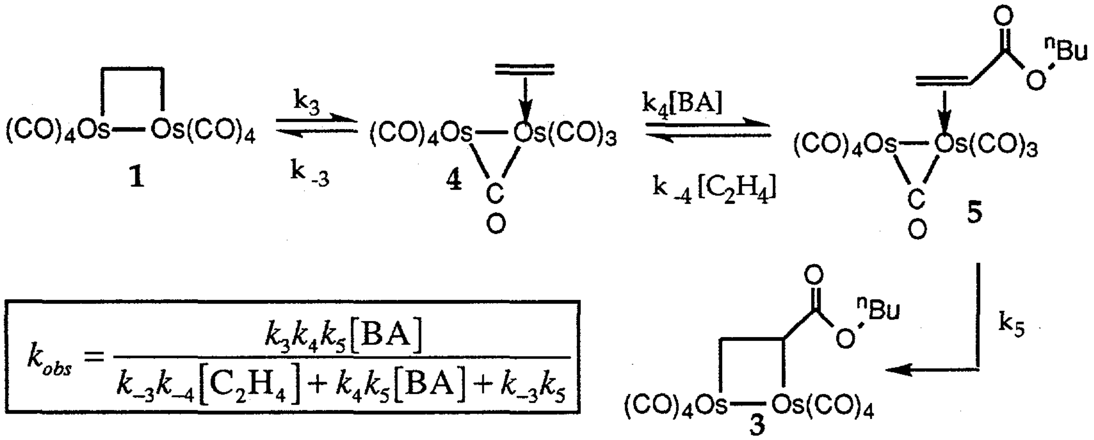
A pair of lengthy full papers that *summarize and conclude our work in this area* have been submitted to *JACS*. (ref 4) "Kinetics of Diosmacyclobutane Exchange Reactions," David L. Ramage, Dawn C. Wiser, and Jack R. Norton*; (ref 5) "Evidence for a Ring Opening Preequilibrium in the Exchange Reactions of Diosmacyclobutanes," Bruce R. Bender, David L. Ramage, Jack R. Norton,* Dawn C. Wiser, and Anthony K. Rappé*. A separate paper, with Bruce Bender as sole author but supported by (and acknowledging) this grant and helpful discussions with the principal investigator, is (ref 6) "An Analysis of the Deuterium Equilibrium Isotope Effect for the Binding of Ethylene to a Transition-Metal Complex," Bruce R. Bender, *J. Am. Chem. Soc.* **1995**, *117*, 11239-11246. A related paper, reporting the structure of an unsubstituted diosmacyclobutane from nematic phase NMR data, is listed in Section **D** below.

The mechanism we believe we have established for the exchange of external olefins or acetylenes into diosmacyclobutanes (i.e., reactions like eq 1) is shown as Scheme I.



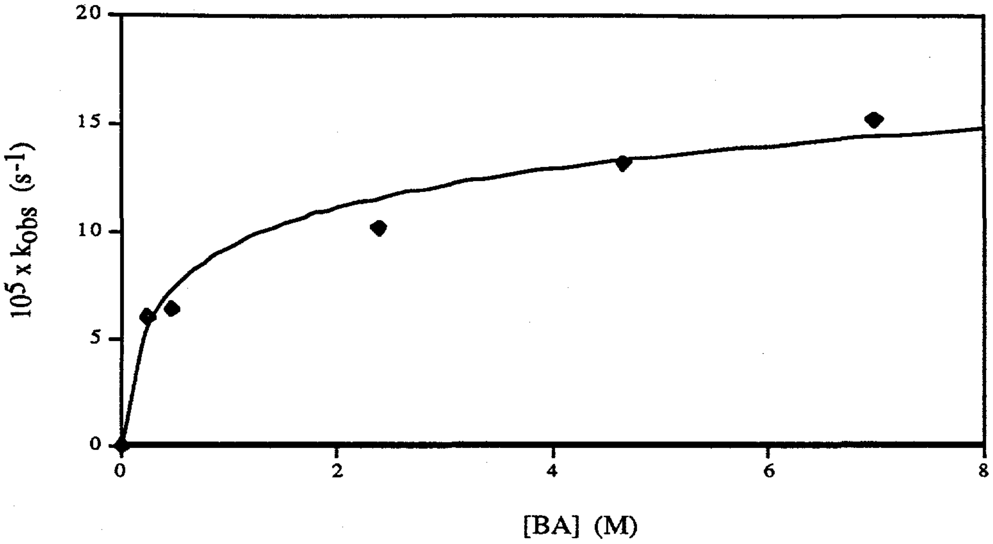
1 3 (1)

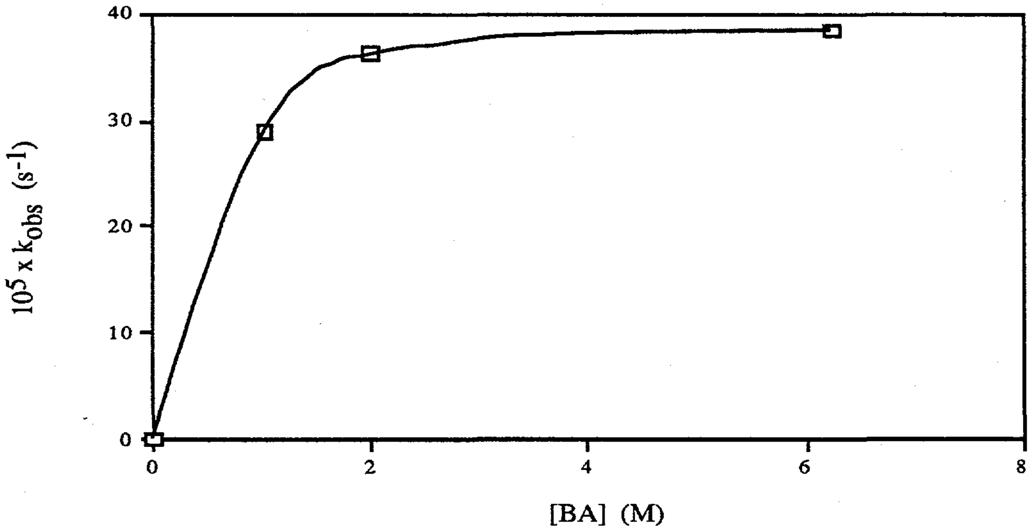
Scheme I

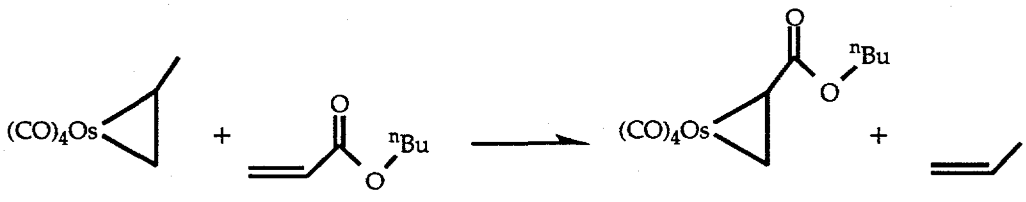


$$k_{obs} = \frac{k_3 k_4 k_5[\mathrm{BA}]}{k_{-3}k_{-4}[\mathrm{C_2H_4}] + k_4 k_5[\mathrm{BA}] + k_{-3}k_5}$$

An additional argument against a dissociative mechanism of any kind comes from the behavior of k_{obs} for the dinuclear reaction 1 as a function of [BA] with no added ethylene (Figure 1a); BA = butyl acrylate. Figure 1b, for eq 2 with no added propene, illustrates the type of saturation behavior to be expected from a classic dissociative mechanism. Because BA is a better ligand than propene for the intermediate $Os(CO)_4$, and because the only propene present is that which has dissociated, k_9[BA] becomes >> k_{-8}[propene] in Scheme II at relatively modest concentrations (about 2M) of added BA; under those conditions k_{obs} approaches k_8 and saturation is observed.

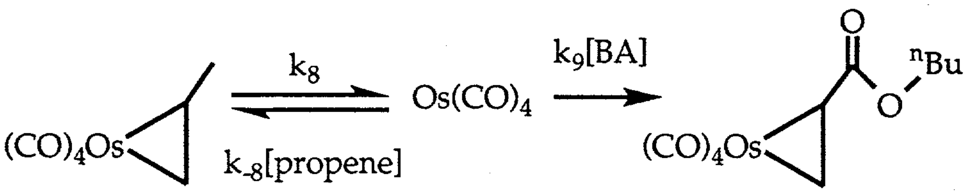

20
15
10
5
0
0
2
4
6
8
10^5 x k_{obs} (s^{-1})
[BA] (M)


40
30
20
10
0
0
2
4
6
8
10^5 x k_{obs} (s^{-1})
[BA] (M)


$(CO)_4Os$
+
O
O
nBu
$(CO)_4Os$
O
O
nBu
+

(2)

Scheme II

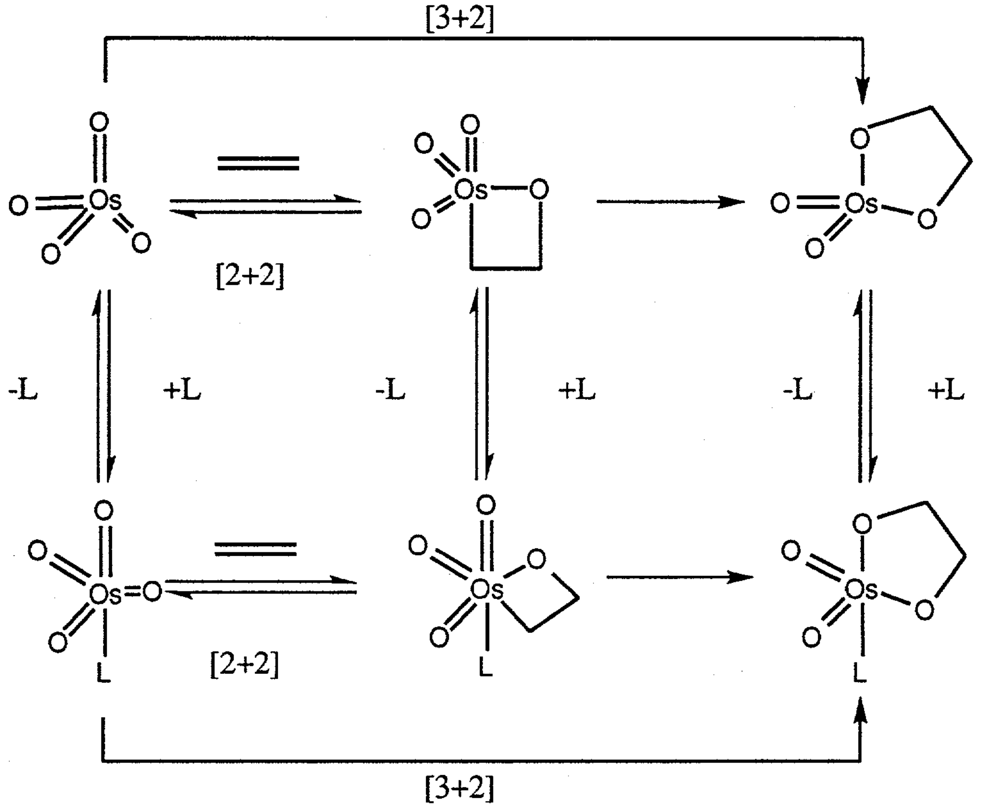


In contrast, in **Scheme I** attack by BA on the ring-opened intermediate **4** (rate constant k_4) competes with an *intramolecular* reaction, the reclosure of the diosmacyclobutane ring (rate constant k_{-3}). It is not clear that the reaction of BA with **4**, rate constant k_4[BA], can ever overwhelm *intramolecular* ring closure, rate constant k_{-3} — even in neat BA.

Dissociation of ethylene from **4**, leading to $Os_2(CO)_8$ (**2**), competes with **Scheme I** when the concentration of the entering olefin or acetylene is extremely low. A trace of $Os_4(CO)_{16}$[10] is observed when $Os_2(CO)_9$ is prepared from $Os_2(CO)_8$(propene) and CO, and when propene is swept out by N_2 gas from a solution of $Os_2(CO)_8$(propene).

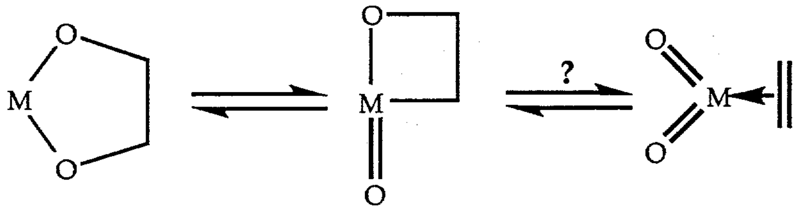
General Implications. A satisfying picture of the formation and fragmentation of metallacycles is beginning to emerge. The exchange reactions of **1** proceed via the ring-opened intermediate **4**, and the exchange reactions of titanacyclobutanes proceed via alkylidene olefin complexes.[11] Kress and Osborn have observed an alkylidene olefin complex at low temperatures;[12] a density functional study by Ziegler and Folga[13] of the formation of molybdacyclobutanes suggests that initial olefin attack is at the metal, forming an alkylidene olefin intermediate. Bennett and Wolczanski have reported olefin rotation — implying a nitrene olefin intermediate — in the azametallacyclobutane prepared from the reaction of C_2H_4 with the transient imido complex $(silox)_2Ti{=}NSi^tBu_3$;[14] similar results have been reported by Horton and co-workers in a vanadaazetine system.[15]

It is tempting to suggest that apparent 2 + 2 organometallic cycloadditions always involve initial coordination of the organic partner to the metal in the organometallic 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.[16] Sharpless and co-workers[16,17] prefer the metallaoxetane [2 + 2] pathway in eq 3; 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} .[17a] Corey and co-workers prefer initial coordination of the alkene to the osmium of the OsO_4, followed by a [3 + 2] cycloaddition (also shown in eq 3); as evidence they point to their ability to explain stereochemical data.[18]



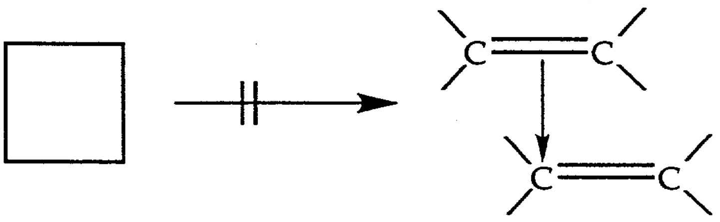
(3)

The results of Phan and Gable[19] imply that osmate esters are *not* formed by direct 3 + 2 cycloadditions between OsO_4 and olefins. A plausible alternative involves the osmaoxetane shown in eq 4. The fact that our diosmacyclobutane **1** is formed from the ring-opened intermediate **4** suggests that the osmaoxetane in eq 4 is formed by ring closure of the analogous polyoxo/alkene complex. Indeed, Nugent has spectroscopically characterized an OsO_4/alkene complex, observable prior to osmate ester formation.[20]



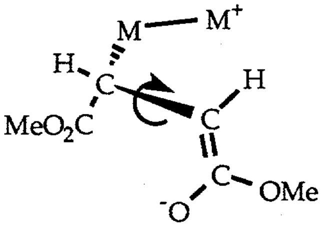
(4)

In order to take advantage of this mechanism for formation and fragmentation *the ring must contain at least one element with d orbitals.* Cyclobutane does not have the luxury of the mechanism in eq 5, and must resort to a *diradical* intermediate instead.



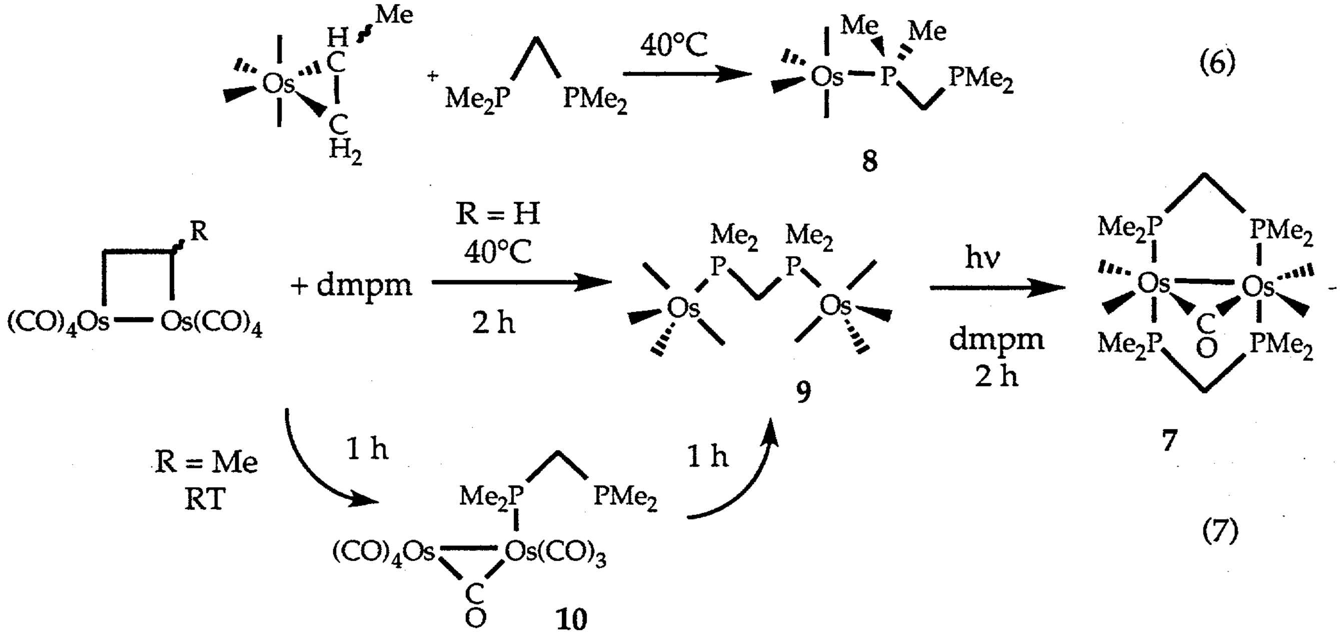
(5)

Formation and Fragmentation of Metallacycles in A-Frame Diosmium and Diruthenium Systems. (not yet submitted for publication) The cis olefin dimethyl maleate (DMM) exchanges with $Os_2(CO)_8(C_2H_4)$ (**1**) *without* loss of stereochemistry. In contrast, Johnson and Gladfelter have found that the closely related compound $Ru_2(CO)_5(dmpm)_2$ (**5**) (dmpm = bis(dimethylphosphino)methane) isomerizes DMM to its trans isomer dimethyl fumarate (DMFum) as it forms a diruthenacyclobutane, $Ru_2(CO)_4(DMFum)(dmpm)_2$ (**6**)[21] analogous to **1**. We have prepared osmium complexes analogous to **5** and have investigated their reactions with DMM. No diosmacyclobutane analogous to **6** is observed in the reaction of $Os_2(CO)_5(dmpm)_2$ (**7**) with a large excess of DMM; free DMM is, however, isomerized catalytically to DMFum. The mechanism by which these electron-rich systems lose stereochemistry probably involves a *zwitterionic* intermediate (like that pictured) rather than a diradical.

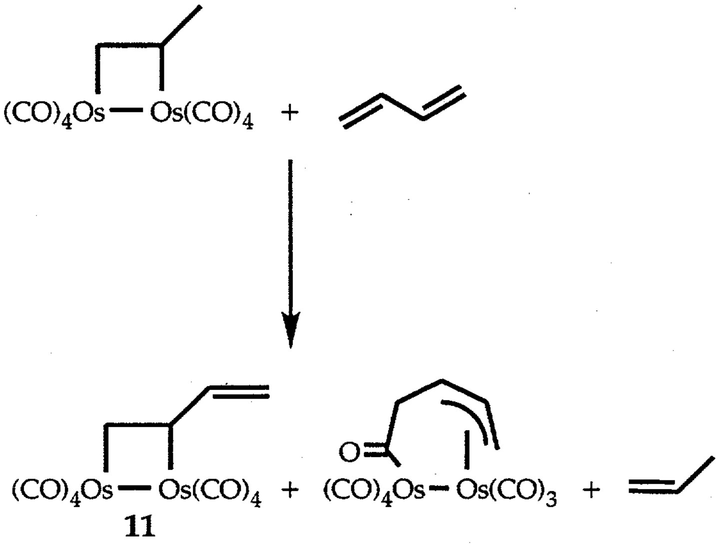


The preparation of **7** and several other Os_2 dmpm complexes is shown in Scheme III. Treatment of **1** with dmpm gives $(CO)_4OsPMe_2CH_2PMe_2Os(CO)_4$ (**9**) quantitatively; photolysis of **9** gives **7** in excellent yield. An intermediate, **10**, analogous to the ring-opened intermediate **4** in diosmacyclobutane exchange reactions is observed in the formation of **9** from $Os_2(CO)_8$(propene).

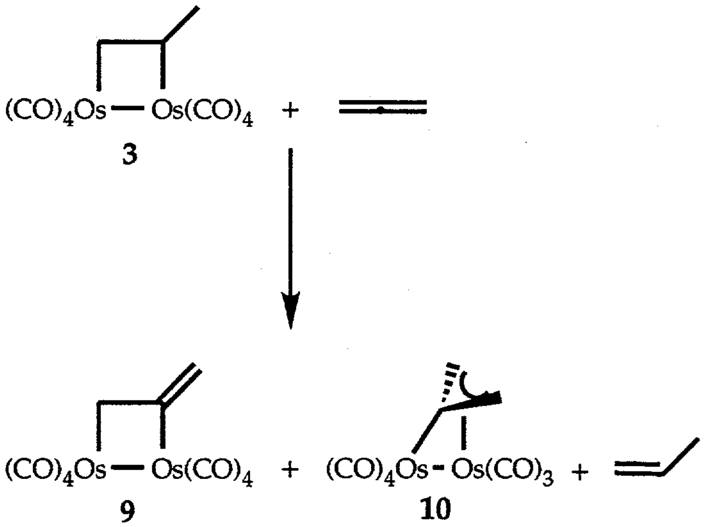
Scheme III



C. Reaction of dienes and allenes with diosmacyclobutanes. A full paper describing this work has appeared: (ref 7) "The Reaction of 1,3- Butadiene and Allene with a Diosmacyclobutane," N. Spetseris and J.R. Norton, *Organometallics*, **1995**, *14*, 603.

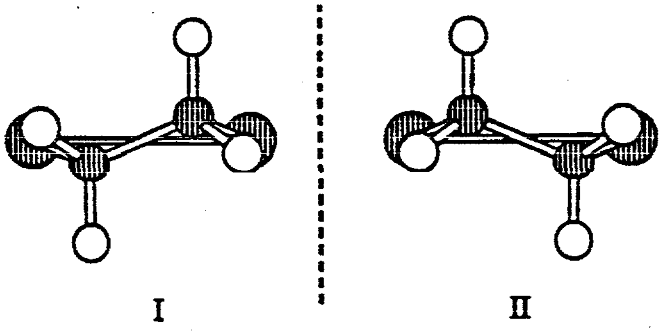


(8)



(9)

D. Determination by Nematic Phase NMR of the Structure of Mononuclear and Dinuclear Ethylene Complexes of Osmium. A manuscript (ref 8), "Ethylene Ligand Geometries of $(C_2H_4)Os(CO)_4$ and $(C_2H_4)Os_2(CO)_8$ Determined by ^1H NMR in Liquid Crystal Solvents," B.R. Bender, R.T. Hembre, and J.R. Norton*, describing the determination of the structures of **1** and of $Os(CO)_4(C_2H_4)$ from nematic phase NMR was submitted for publication to *Inorganic Chemistry* and favorably reviewed; however, some comments by one reviewer (Elliott Burnell, U. of British Columbia) led to collaboration and additional work. The final modifications have been drafted and should be at *Inorganic Chemistry* shortly. The structural parameters obtained in this way for **1** are quite close to those obtained previously from a single-crystal neutron diffraction study.[22]

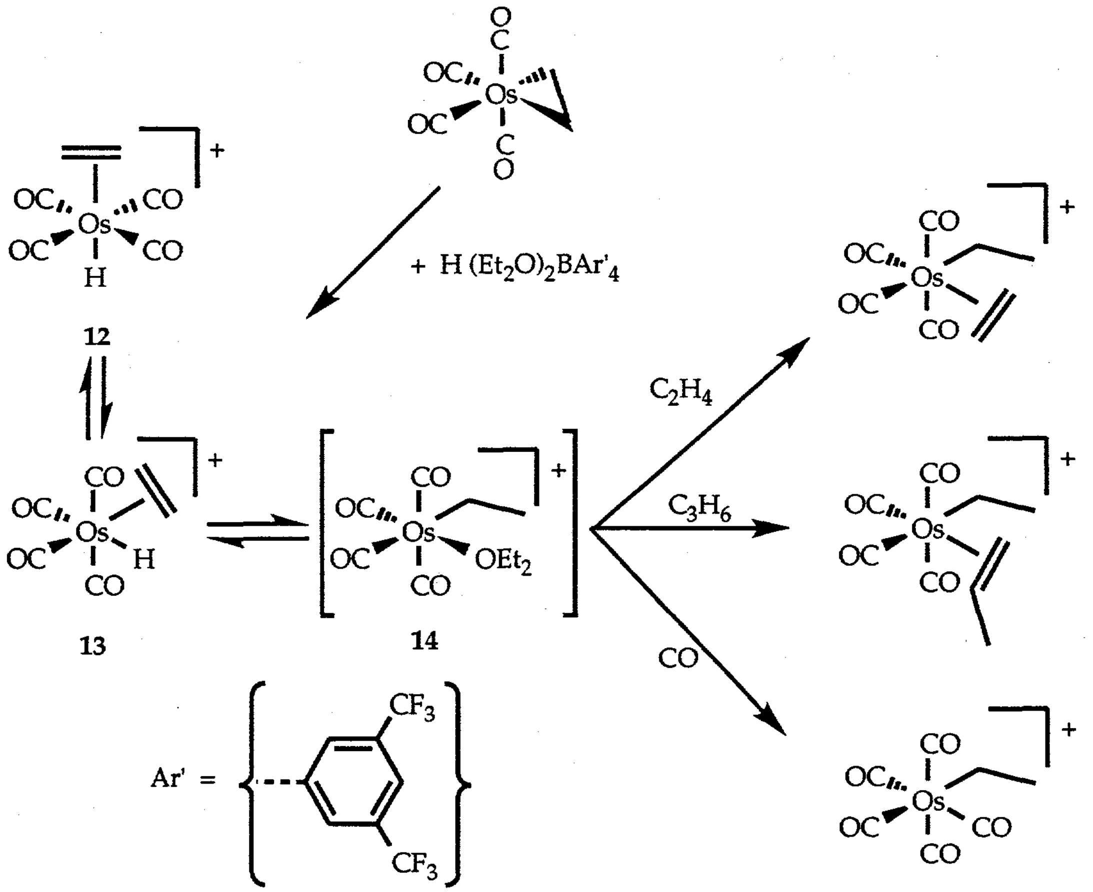


Structure of the Two Enantiomeric Conformations I and II of 1 (C_2 Symmetry)

E. Generation of "Coordinatively Unsaturated" Complexes by Protonation of Methyl Osmium Complexes. A manuscript on this work (described in Ph.D. thesis, Nikolaos Spetseris, 1995) is in preparation (ref 9).

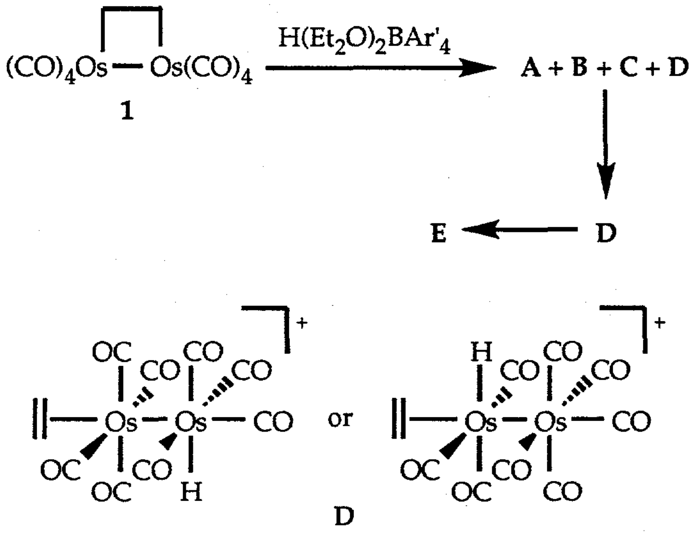
The mononuclear ethylene complex below is best described as an osmacyclopropane.[23] Its protonation with the "Brookhart acid"[24] (see Scheme IV below) leads to an equilibrating mixture of cationic trans- and cis-ethylene hydrides (**12** and **13** respectively) and the ethyl complex **14**. Olefins and CO trap **14**, but no evidence is seen for oligomerization or CO insertion at 0°C and moderate pressures (< 100 psig).

Scheme IV



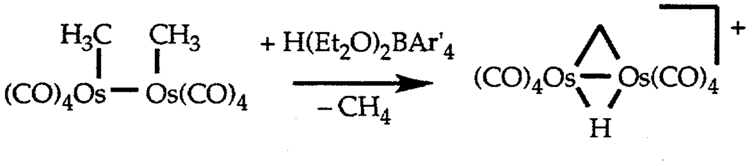
In an effort to prepare the methyl analogs of **12**, **13**, and **14** we have protonated $Os(CO)_4Me_2$. With $HBF_4 \bullet Et_2O$ we get *cis*-$(OC)_4Os(FBF_3)CH_3$, just reported by Beck and co-workers;[25] with $H(OEt_2)_2BAr'_4$ we get a mixture of cis and trans cationic ether complexes.

We have also studied the protonation of **1** and related dinuclear compounds. When **1** is treated with the "Brookhart acid," it forms a mixture of **A**, **B**, **C**, and **D** (eq 10), all possessing hydride ligands and C_2H_4 ligands that are *π–bound* and not 1,2-di-σ bound as in **1**. A single crystal X-ray diffraction study of D indicated that its C_2H_4 ligand occupies an apical site. Disorder precluded finding the hydride, but it presumably occupies one of the eight equatorial sites.



(10)

Protonation of $Me_2Os_2(CO)_8$ leads to elimination of CH_4 and formation of the methylene hydride complex (**15**) (eq 11); an equilibrium is slowly established between **15** and two cationic methyl ether Os_2 complexes. Compound **15** can also be prepared by protonation of the neutral methylene complex.



15

(11)

---

[1] "[(η^2-C_2H_4)Os(CO)$_4$] as a Vibrational Model for Surface Type I' Ethene Chemisorbed as a Metallacyclopropane on Metal Surfaces," C.E. Anson, N. Sheppard*, D.B. Powell, B.R. Bender and J.R. Norton, *J. Chem. Soc., Faraday Trans.*, **1994**, *90*, 1449-1454.

[2] "Assignments of the Infrared and Raman Spectra of the $Os_2(\mu_2$-$CHCH_3)$ Group of [μ_2-$CHCH_3$) Os_2 (CO)$_8$] and of their **d^1** and **d^4** Isotopologues as Models for the Spectrum of such Ethylidene Groups on Metal Surfaces," C.E. Anson, N. Sheppard*, D.B. Powell, J.R. Norton*, W. Fischer, R.L. Keiter, B.F.G. Johnson, J. Lewis, A.K. Bhattacharrya, S.A.R. Knox, and M.L. Turner, *J. Am. Chem. Soc.* **1994**, *116*, 3058-3062.

[3] "Retention of Stereochemistry in the Formation and Fragmentation of Diosmacyclobutanes, and Other Evidence Against a Diradical Mechanism," R.T. Hembre, D.L. Ramage, C.P. Scott and J.R. Norton*, *Organometallics* **1994**, *13*, 2995-3001.

[4] "Kinetics of Diosmacyclobutane Exchange Reactions," David L. Ramage, Dawn C. Wiser, and Jack R. Norton*; (ref 5) "Evidence for a Ring Opening Preequilibrium in the Exchange Reactions of Diosmacyclobutanes," Bruce R. Bender, David L. Ramage, Jack R. Norton,* Dawn C. Wiser, and Anthony K. Rappé*.

[5] "Evidence for a Ring Opening Preequilibrium in the Exchange Reactions of Diosmacyclobutanes," Bruce R. Bender, David L. Ramage, Jack R. Norton,* Dawn C. Wiser, and Anthony K. Rappé*.

[6] "An Analysis of the Deuterium Equilibrium Isotope Effect for the Binding of Ethylene to a Transition-Metal Complex," Bruce R. Bender, *J. Am. Chem. Soc.* **1995**, *117*, 11239-11246.

[7] "The Reaction of 1,3- Butadiene and Allene with a Diosmacyclobutane," N. Spetseris and J.R. Norton, *Organometallics*, **1995**, *14*, 603.

[8] "Ethylene Ligand Geometries of (C_2H_4)Os(CO)$_4$ and (C_2H_4)Os_2(CO)$_8$ Determined by ^{1}H NMR in Liquid Crystal Solvents," B.R. Bender, R.T. Hembre, and J.R. Norton*.

[9] "Coordinatively Unsaturated" Complexes by Protonation of Methyl Osmium Complexes. A manuscript on this work (described in Ph.D. thesis, Nikolaos Spetseris, 1995) is in preparation.

---

[10] Johnson, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 8111.

[11] (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.

[12] Kress, J.; Osborn, J. A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1585-1587.

[13] Folga, E.; Ziegler, T. *Organometallics* **1993**, *12*, 325.

[14] Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179-2180.

[15] de With, J.; Horton, A. D.; Orpen A. G. *Organometallics* **1993**, *12*, 1493-1496.

[16] (a) Kolb, H. C.; Andersson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 1278-1291, and references therein. (b) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, 2483. (c) Berisford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **1995**, *34*, 1059-1070.

[17] (a) Göbel, T.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1329-1331. (b) Norrby, P.-O.; Becker, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1996**, *118*, 35-42.

[18] Corey, E. J.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 319-329, and references therein.

[19] (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.

[20] Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 4533-4534.

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

[22] "A Single Crystal Neutron Diffraction Study of $(\mu-\eta^1,\eta^1-C_2H_4)Os_2(CO)_8$, 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.

[23] Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappé, A. K. *Organometallics* **1992**, *11*, 3427.

24 Brookhart, M; Grant, B.; Volpe, A. F. **1992**, *11*, 3920.

[25] Rosendorfer, P.; Mihan, S.; Niemer, B.; Beck, W. Z. *Naturforsch.* **1995**, *50b*, 1759-1766.