Retention of Stereochemistry in the Formation and Fragmentation of Diosmacyclobutanes, and Other Evidence against a Diradical Mechanism

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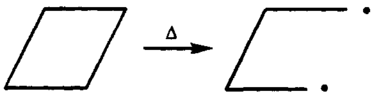
Two results argue against a diradical intermediate in the exchange of diosmacyclobutanes with free olefins. The diosmacyclobutane $Os_2(CO)_8(\mu\text{-propene})$ reacts with vinylcyclopropane to give as the sole product a diosmacyclobutane bearing an intact cyclopropane ring. Repeated exchange of *trans*-ethylene-*1,2*-d_2 with the same ligand in a diosmacyclobutane shows >99.1% stereochemical excess per exchange half-life. These exchange reactions do not involve mononuclear olefin complexes.

Introduction

The isolobal relationship[1] between the diosmacyclobutane $Os_2(CO)_8(\mu\text{-}C_2H_4)$ (**1**) and cyclobutane suggests investigation of the stereochemistry with which ethylene is lost from **1**. As the fragmentation of cyclobutane is known to proceed through the tetramethylene diradical **2** (eq 1),[2] it is worth asking whether the fragmentation of **1** involves the diradical **3** (eq 2).



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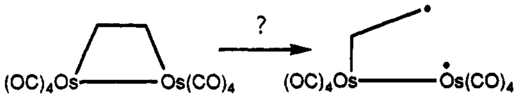
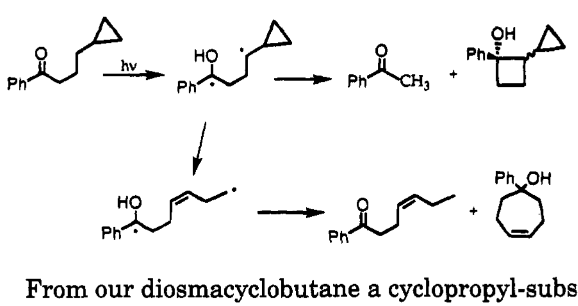
(1)



1 3

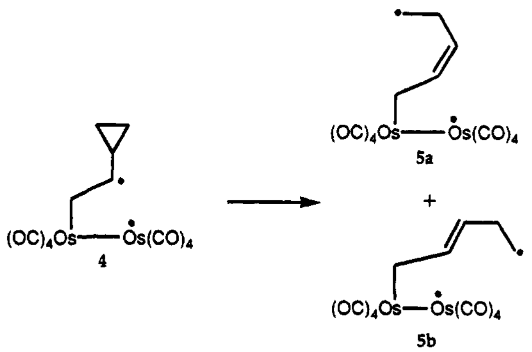
(2)

One way of testing for a diradical intermediate like **3** is the introduction of a cyclopropyl substituent on the putative radical center. The formation of a primary radical by opening the three-membered ring will lead to alternative products, as in the Norrish type II photoreaction in eq 3.[3]



(3)

From our diosmacyclobutane a cyclopropyl-substituted diradical **4** should give a mixture of the primary radicals **5a** and **5b** (eq 4). The related methyl-substituted radical **6** is known to open to a mixture of the *Z* radical **7a** and the *E* radical **7b** with a rate constant of 4×10^7 s^{-1} at 25 °C.[4]



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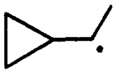
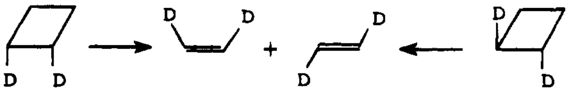


6

7a

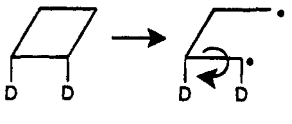
7b

A more sensitive test for diradical intermediates is the loss of stereochemistry by rotation about the C_1–C_2 bond. Chickos has reported (eq 5)[5] that the thermolysis of both (1*R*,2*S*) and (1*R*,2*R*)-cyclobutane-*1,2*-d_2 yields the same 50:50 mixture of *cis*- and *trans*-ethylene-*1,2*-d_2.



(5)

Such loss of stereochemistry is expected for the diradical shown in eq 6.



(6)

The use of deuterium substitution allows the stereochemistry to be monitored at a primary radical center while ensuring the prompt loss of stereochemistry by

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1994.

[1] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[2] Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982.

[3] (a) Wagner, P. J.; Liu, K.-C.; Noguchi, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3837. (b) Wagner, P. J.; Park, B.-S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11.

[4] (a) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

[5] (a) Chickos, J. S.; Annamalai, A.; Keiderling, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 4398. (b) Chickos, J. S. *J. Org. Chem.* **1979**, *44*, 780.

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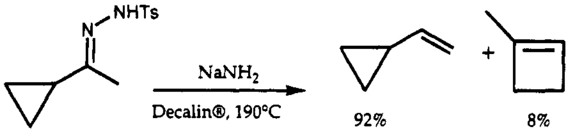
the diradical intermediate.[6] "Memory" effects are known to hinder rotation (and loss of stereochemistry) relative to cleavage in diradicals with 1,2-dimethyl substitution[7a] and with phenyl,[7b] diphenyl,[7c] or cyano[7d] substituents.

We have previously shown substantial retention of stereochemistry in the extrusion of HDC=CHD from *cis*- and *trans*-**1**-d_2.[8] As it is important to distinguish *substantial* retention (which is possible with a diradical mechanism) from *complete* retention (which is not), we now wish to report a more precise measurement of the extent of retention than the one communicated several years ago.[8] Our method arises from the fact that exchange between the ethylene in **1** and free ethylene is reversible,[8] so that under appropriate conditions any loss of stereochemistry will be amplified by repeated reaction. The method finds precedent in the use of a reversible cyclobutene–butadiene electrocyclic reaction by Doorakian and Freedman in 1968 to check for *any* reaction by a symmetry-forbidden path.[9]

We also report the stereochemical outcome of a number of other reactions in which HDC=CHD is introduced into—or extruded from—diosmacyclobutanes.

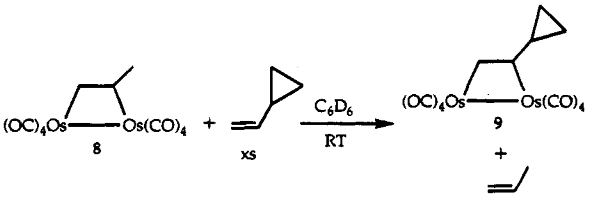
Results

Vinylcyclopropane, prepared by the method of Rudolph and Weedon (eq 7),[10] contained 8% 1-methylcyclobutene.



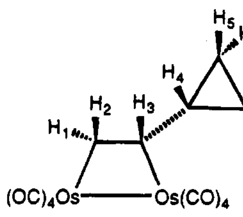
(7)

An excess of this vinylcyclopropane/methylcyclobutene mixture displaced propylene cleanly from the methyl-substituted diosmacyclobutane **8** at room temperature (eq 8).



(8)

The only product detected (>90% NMR yield) was **9**, with the characteristic chemical shifts (0.85 through −0.22 ppm) of an intact cyclopropane ring. Eight separate resonances were observed in the ^{1}H NMR spectrum of **9**; protons H_5 and H_7 are diastereotopic, as are protons H_6 and H_8, and protons H_1 and H_2. The resonances for H_1–H_4 were assigned unambiguously from the ^{1}H–^{1}H COSY spectrum of **9**, and pairs of resonances could be assigned to H_5 and H_7, and to H_6 and H_8, although it was not possible to make absolute assignments in those cases. The infrared spectrum of **9**, virtually identical with that of **8**, is typical of the spectra of diosmacyclobutanes.



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While it is impossible to be sure of the rate constant for rearrangement of the cyclopropyl-substituted diradical **4** to **5a** and **5b** (eq 4), it is surely $>10^6$ s^{-1} and probably $>10^7$ s^{-1}. Substituent effects on such rate constants are not large: at 25 °C that for the unsubstituted cyclopropylmethyl radical is 9.4×10^7 s^{-1},[4b] that for **6** (the closest analog to **4**—see above) is 4×10^7 s^{-1},[4] and that for **10** is 5×10^7 s^{-1}.[4] Our results certainly exclude a diradical intermediate with a lifetime greater than 10^{-6} s.

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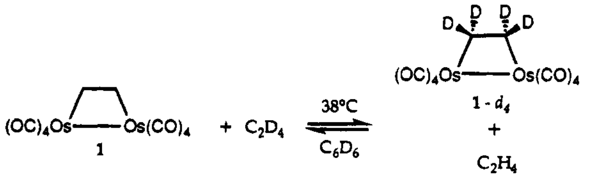
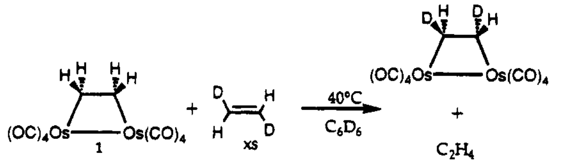
Exchange between 1 and Free Ethylene. The bound ethylene in **1** exchanged with C_2D_4 in a few hours at 38 °C (eq 9).

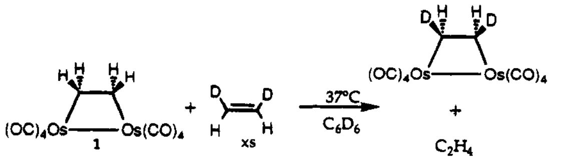


(9)

Stereochemistry of Exchange with Ethylene-*1,2*-d_2. Similar exchange was observed with *trans*- and *cis*-ethylene-*1,2*-d_2 (eqs 10 and 11). In both cases nematic-phase ^{1}H NMR showed[11] at least 90% of the product to have the same stereochemistry as the initial olefin.



(10)



(11)

Gas-phase IR analysis[12] of the ethylene-*1,2*-d_2 evolved in eq 12 again showed predominant retention of stereochemistry.

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[6] Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863.

[7] (a) Dervan, P. B.; Uyehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069. (b) Koniz, R. F. Ph.D. Thesis, Cornell University, 1980. (c) Jones, G.; Chow, V. L. *J. Org. Chem.* **1974**, *39*, 1447. (d) Doering, W. von E.; Guyton, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 3229.

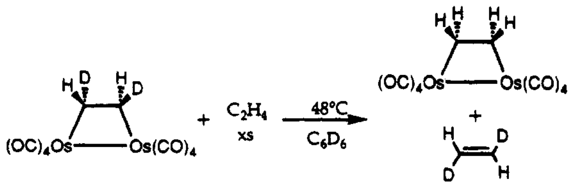
[8] Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468.

[9] Doorakian, G. A.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 5310; **1968**, *90*, 6896 (correction). The authors are grateful to Prof. Dennis Dougherty for bringing this precedent to their attention.

[10] Rudolph, A.; Weedon, A. C. *Can. J. Chem.* **1990**, *68*, 1590.

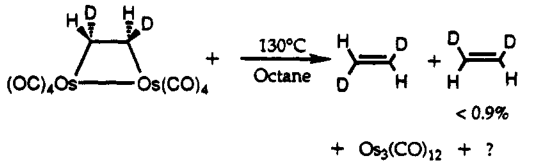
[11] The assessment of stereochemistry in these compounds, and the determination of their structure, by ^{1}H NMR in nematic phase solvents will be reported separately: Bender, B. R.; Hembre, R. T.; Norton, J. R. Manuscript in preparation.

[12] (a) Golike, R. C.; Mills, I. M.; Person, W. B.; Crawford, B., Jr. *J. Chem. Phys.* **1956**, *25*, 1266. (b) Rochkind, M. M. *Anal. Chem.* **1968**, *40*, 762.



(12)

The same was true of the ethylene-*1,2*-d_2 evolved from the thermolysis of *trans*- and *cis*-**1**-*3,4*-d_2 (eqs 13 and 14).



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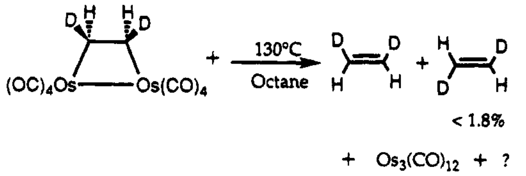
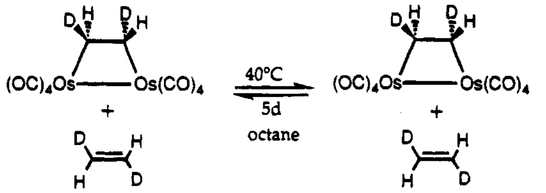


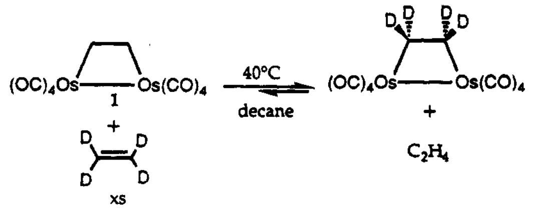
(14)

Quantification of Stereochemical Retention during Exchange between 1 and Free Ethylene. An octane solution of *trans*-**1**-*3,4*-d_2 was stirred under a substantial excess of *trans*-ethylene-*1,2*-d_2 for 6 days at 40 °C, producing the degenerate exchange shown in eq 15. (The *trans* stereoisomer of free and bound ethylene-*1,2*-d_2 was used because the product that would arise from loss of stereochemistry, *cis*-ethylene-*1,2*-d_2, has a larger extinction coefficient[12] and can be more precisely quantified than its *trans* counterpart.) The excess of *trans*-ethylene-*1,2*-d_2 suppressed the decomposition of the diosmacyclobutane that would otherwise have occurred under these conditions. IR monitoring of the ethylene atmosphere showed little conversion to *cis*-ethylene-*1,2*-d_2 for 5 days; increasingly rapid isomerization of the ethylene-*1,2*-d_2 was observed after that time.



(15)

The exchange half-life of the diosmacyclobutane in reaction 15 was determined by measuring the half-life for loss of C_2H_4 from **1** in the presence of excess C_2D_4 under the same conditions (eq 16). Because kinetic studies[13] have shown that the rates of such exchanges depend upon the concentration of the entering olefin, $[C_2D_4]$ in eq 16 was kept the same as [*trans*-HDC=CHD] in eq 15.



(16)

The observed rate constant, $1.06(1) \times 10^{-4}$ s^{-1}, implied an exchange half-life of 109(1) min for *trans*-**1**-*3,4*-d_2 in reaction 15. The observation of $<1.0 \times 10^{-6}$ mol of *cis*-ethylene-*1,2*-d_2 in 5 days (66.1 half-lives) implied $<1.5 \times 10^{-8}$ mol/half-life. As 6.3×10^{-6} mol of *trans*-**1**-*3,4*-d_2 would have released 3.2×10^{-6} mol of *trans*-ethylene-*1,2*-d_2 in 1 half-life, the loss of stereochemistry was <0.43% and the stereochemical excess was >99.1%.[14]

Retention of this magnitude has been reported in other cycloaddition reactions. For example, Huisgen has reported[15] that diazomethane cycloadds to methyl angelate and tiglate with >99.94% and >99.997% stereospecificity, and Houk and co-workers have found that *cis*- and *trans*-ethylene-*1,2*-d_2 add to *p*-nitrobenzonitrile oxide with >98% stereospecificity and to butadiene with >99% stereospecificity.[16]

Firestone has argued that even such exceptionally high stereospecificities do not rule out diradical mechanisms, on the grounds that (1) the rotation barriers in such diradicals could exceed those in known radicals and (2) cyclization of diradicals could be much faster than the combination of radicals in solution.[17] These suggestions are particularly plausible for an unknown radical like **3**. However, we believe that our failure to observe *any* ring opening with vinylcyclopropane, and the high degree of stereoretention reported in this manuscript, make a diradical mechanism *highly unlikely* for the exchange of diosmacyclobutanes with free olefins. Even the *loss* of stereochemistry reported by Johnson and Gladfelter for the formation of diruthenacyclobutanes from maleates and fumarates[18] is, we believe, due to the zwitterionic mechanism proposed by these workers and not to a diradical one.

The small but finite loss of stereochemistry when *trans*-**1**-*3,4*-d_2 is stirred under excess *trans*-ethylene-*1,2*-d_2 is probably not intrinsic to reaction 15 but rather catalyzed by small amounts of diosmacyclobutane *decomposition products*. The residue left after the 130 °C thermolysis of *trans*-**1**-*3,4*-d_2 (reaction 12) proved to be an efficient catalyst not only for the stereomutation of ethylene but for intermolecular H/D exchange (eq 17). The catalyst in reaction 17 is probably an osmium hydride; $H_2Os_3(CO)_{10}$ is known to react with ethylene and to scramble rapidly the deuterium in *trans*-ethylene-*1,2*-d_2.[19]

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(13) Ramage, D. L.; Wiser, D.; Norton, J. R. Manuscript in preparation.

(14) Since any diradical intermediate that was formed would be expected to extrude a 50/50 mixture of *cis*- and *trans*-ethylene-d_2's, the stereochemical excess is calculated as follows:

stereochemical excess > 100 − 2 ×

$$100\left(\frac{1.0 \times 10^{-6}\text{ mol of }cis\text{-ethylene-}1,2\text{-}d_2/66.1\text{ half-lives}}{3.2 \times 10^{-6}\text{ mol of }trans\text{-}\mathbf{1}\text{-}3,4\text{-}d_2}\right)\%$$

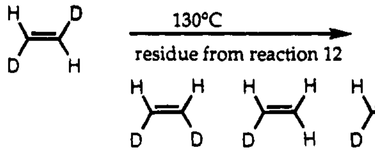
(15) Bihlmaier, W.; Geittner, J.; Huisgen, R.; Reissig, H.-U. *Heterocycles* **1978**, *10*, 147.

(16) (a) Houk, K. N.; Firestone, R. A.; Munchausen, L. L.; Mueller, P. H.; Arison, B. H.; Garcia, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 7227. (b) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554.

(17) Firestone, R. A. *Heterocycles* **1987**, *25*, 61.

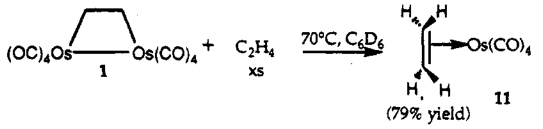
(18) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1991**, *10*, 376.

(19) Ferrari, R. P.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta* **1978**, *31*, 177.



(17)

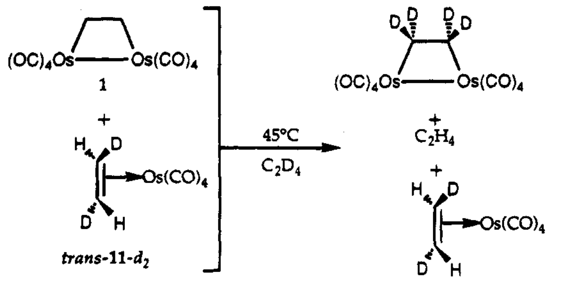
Exchange between 1 and Free Ethylene Does *Not* Involve the Mononuclear Ethylene Complex 11. Prolonged heating with excess olefin converts diosmacyclobutanes to the corresponding mononuclear olefin complexes. For example, **1** was converted to $Os(CO)_4(C_2H_4)$ (**11**)[20,21] by excess ethylene slowly at 70 °C and rapidly at 100 °C (eq 18).



(18)

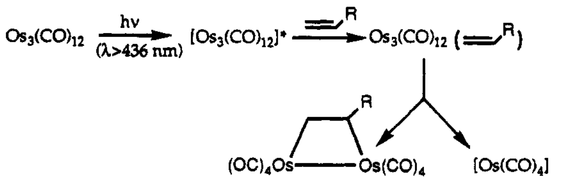
Such mononuclear olefin complexes themselves exchange with free olefin, albeit more slowly than the corresponding diosmacyclobutanes. For example, little C_2H_4 was released when the mononuclear ethylene complex **11** was treated with an excess of C_2D_4 for 2 h at 70 °C.

It nevertheless seemed worthwhile to investigate the possibility that mononuclear olefin complexes could catalyze exchange between free olefins and diosmacyclobutanes. A solution containing both **1** and (*trans*-$C_2D_2H_2$)$Os(CO)_4$ (*trans*-**11**-d_2) was heated under C_2D_4 (eq 19). After 4 h at 45 °C, C_2H_4 was the only new ethylene observed in the atmosphere of C_2D_4—implying that **11** was not an intermediate in the exchange between **1** and free ethylene.



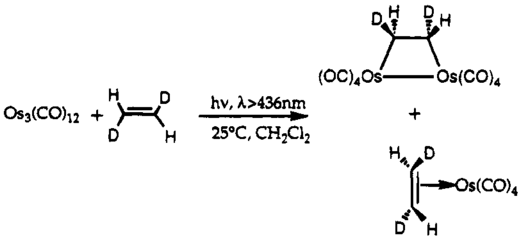
(19)

Photochemical Exchange of 1 with Free Ethylene. The photochemical reaction of olefins and alkynes with $Ru_3(CO)_{12}$ has provided a valuable route to mononuclear ruthenium complexes.[22] The Takats,[21] Poë,[23] and Wrighton[24] groups have shown that the photochemical reaction of $Os_3(CO)_{12}$ with alkenes yields both mono- and diosmium complexes, and the Takats group has described the more limited photochemical reaction with alkynes.[25] Poë has proposed a mechanism that involves addition of the alkene or alkyne to a photoactivated $[Os_3(CO)_{12}]^*$ intermediate (eq 20).[23]



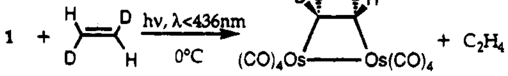
(20)

If this intermediate reacts with alkenes without *cis*/*trans* isomerization, the photochemical reaction of *cis*- and *trans*-ethylene-*1,2*-d_2 with $Os_3(CO)_{12}$ should offer a direct approach to the preparation of *cis*- and *trans*-**1**-*3,4*-d_2. We therefore photolyzed $Os_3(CO)_{12}$ with *trans*-ethylene-*1,2*-d_2 (eq 21) under conditions (λ > 436 nm)[26] equivalent to those used by Poë and found[11] that both the mono- and diosmium products had been formed with retention of stereochemistry.



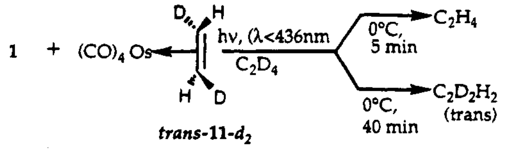
(21)

When a solution of **1** was exposed only to low energy irradiation (λ > 436 nm), it did not exchange with excess C_2D_4. However, irradiation with unfiltered light from a Hg-vapor lamp led to rapid exchange. Irradiation of **1** at 0 °C in the presence of *trans*-ethylene-*1,2*-d_2 formed *trans*-**1**-*3,4*-d_2 exclusively (eq 22). No fragmentation to mononuclear products was observed by IR spectroscopy at short photolysis times (90 min).



(22)

The retention of stereochemistry in this photochemically induced ethylene exchange is surprising in light of the *cis*/*trans* isomerization observed in similar reactions, e.g., the irradiation of dirhenium alkenyl complexes.[27] An additional surprise was the evolution only of C_2H_4 when a mixture of undeuterated **1** and *trans*-**11**-d_2 was irradiated for 5 min under an atmosphere of C_2D_4. Further irradiation (>30 min) led to the evolution of *trans*-ethylene-*1,2*-d_2, without *cis*/*trans* isomerization (eq 23).



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(20) (a) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955. (b) Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1989**, *122*, 1403. (c) Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappé, A. K. *Organometallics* **1992**, *11*, 3427.

(21) Burke, M. R.; Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092.

(22) Takats, J.; Grevels, F.-W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1981**, *103*, 4069.

(23) Poë, A. J.; Sekhar, C. V. *J. Am. Chem. Soc.* **1986**, *108*, 3673.

(24) Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4518.

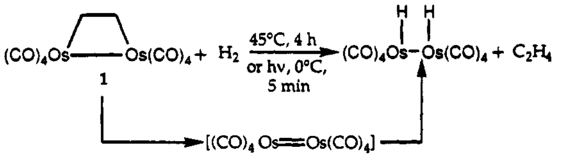
(25) (a) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25. (b) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918.

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

(27) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 3474.

The ethanediyl bridge of **1** appears to be more labile than the ethylene ligand of **11** under both photochemical and thermal conditions.

Addition of Dihydrogen to 1. In view of the long standing interest in the reaction of H_2 with bimetallic complexes,[28] we examined the reaction of H_2 with **1**. Both the thermal and photochemical addition of H_2 were observed (eq 24) under conditions identical to those required for the exchange of ethylene with **1** above.



(24)

Experimental Section

General Considerations. Reactions and manipulations were performed under an atmosphere of nitrogen (high purity, 99.995%) purified by passage through BTS catalyst (BASF) and molecular sieves (3Å, Linde). Measured amounts of gases and volatile organometallic compounds were transferred in vacuo and stored in vacuum-line bulbs or sealed 5-mm NMR tubes (sealed under vacuum, $P < 10^{-3}$ Torr). $Na_2[Os(CO)_4]$ was stored and handled in a nitrogen atmosphere box. Where indicated, solutions were degassed by freezing at −196 °C, evacuating, and thawing three times.

A water-cooled Hanovia 679-Å high-pressure quartz Hg-vapor lamp (450 W, 3.6 A, 175.8-W total radiated energy) was used in photochemical preparations. A saturated $NaNO_2$ solution (aqueous) (10−11 M, 1-cm path length), which filters light below 436 nm, was used as indicated. Hydrogenations were carried out in a 75-mL Fischer-Porter pressure vessel. Preparative TLC was performed under a flow of nitrogen on a Harrison Research Inc. Chromatotron with 2-mm silica plates, or on 2-mm × 20-cm × 20-cm TLC plates (Merck, Kiesel gel, 60).

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer with either a Perkin-Elmer 3600 data station for spectral storage and subtraction or an IBM PC running OLIS PE983 software. Atmospheric bands and DCl were used as instrument calibrants; wavenumber values are within ±0.5 cm^{-1}. Gas-phase spectra were obtained using a 10-cm path length cell with KCl windows and an internal volume of 153 mL or in a similar cell with an internal volume of 199 or 200 mL, depending upon the size of the reaction vessel attached to the side arm.

NMR spectra were recorded on IBM WP-270-SY (^{13}C and ^1H spectra) and WP-200-SY (^1H spectra) spectrometers. Solvent adsorptions were used as internal standards {δ $^1H(^{13}C)$: C_6D_5H, $\delta = 7.15$; $CDHCl_2$, $\delta = 5.32$ (53.8)} in ^1H and ^{13}C spectra. A computer program provided by IBM instruments, Inc., known as parameter adjustment in NMR by iteration calculation (PANIC) was used for spectral simulation on an Aspect 2000 computer or the computer program "NMR" (Calleo Scientific Software Publishers) was used on a Macintosh Centris 650.

Solvents. Ether, octane, hexane, decane, and pentane were distilled under nitrogen or vacuum from Na or K/benzophenone. Methylene chloride was distilled from P_4O_{10}, and C_6D_6 from "titanocene" or from Na/benzophenone. E. Merck Licristal TNC-1565 was degassed on the high vacuum line at 25 °C and used without further purification.

Standard Reagents. $Os_3(CO)_{12}$ was prepared, as previously described,[29] in a 300-mL Autoclave Engineers autoclave. The diosmacyclobutanes **1**[20,24] and $Os_2(CO)_8$(propene) (**8**)[30] were prepared by literature methods. C_2D_4 was purchased from Cambridge Isotope Laboratories and purified by treatment with 0.75 M *n*-BuLi in hexane and P_4O_{10}. *cis*- and *trans*-ethylene-*1,2*-d_2 were synthesized by the methods of Nicholas and Carroll.[31] Osmium tetraoxide was generously provided by Colonial Metals, Inc. and Degussa Corp. Prepurified hydrogen (99.995%) was used without further treatment. Ethylene and propene (polymer grades) were used as received.

Reaction of $Os_2(CO)_8$(propene) (8) with Vinylcyclopropane. A solution of **8** (19.2 mg, 2.97 × 10^{-2} mmol) was prepared in C_6D_6 (0.5 mL), a large excess of vinylcyclopropane/1-methylcyclobutene (92:8 by ^1H NMR)[10] was added, and the reaction mixture was kept at ambient temperature and monitored periodically by ^1H NMR. Resonances assignable to the starting propene complex smoothly disappeared, while resonances assignable to free propene and to the vinylcyclopropane complex **9** appeared (>90% by integration *vs* resonance of starting material). No evidence was seen for any other products or for any reaction of the starting complex with 1-methylcyclobutene. After 16 h, the NMR tube was opened and the reaction mixture was applied to a preparative TLC plate and chromatographed with pentane. Two bands were observed: the first was **9** (12.3 mg, 1.83 × 10^{-2} mmol, 62%), and the second was a trace of $Os_3(CO)_{12}$ (a product of decomposition).

9: ^1H NMR (C_6D_6) δ 2.00 (1H, dd, $^2J_{HH} = -9.9$ Hz, $^3J_{HH} = 7.6$ Hz, H_2), 1.27 (1H, dd, $^2J_{HH} = -9.9$ Hz, $^3J_{HH} = 12.7$ Hz, H_1), 0.99 (1H, ddd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 12.7$ Hz, $^3J_{HH} = 10.1$ Hz, H_3), 0.86 (1H, m, $^3J_{HH} = 10.1$ Hz, H_4), 0.53 (1H, m, H_5 or H_7), 0.46 (1H, m, H_5 or H_7), 0.04 (1H, m, H_6 or H_8), −0.22 (1H, m, H_6 or H_8). Assignments of resonances to either H_5 or H_7, or H_6 or H_8, were made on the basis of strong coupling (H_5 or H_7), or weak coupling (H_6 or H_8), to H_4 in the $^1H-^1H$ COSY spectrum of **9**. The numbering scheme is that depicted in the struction of **9** drawn in the Results. IR: (pentane) 2120 (vw), 2076 (m), 2037 (w, sh), 2030 (vs), 2010 (m), 1995 (w) cm^{-1}; (CH_2Cl_2) 2120 (vw), 2075 (s), 2028 (vs), 2005 (m), 1989 (w) cm^{-1}.

(μ-1,2-Ethanediyl)octacarbonyldiosmium-d_4, 1-d_4. Ethylene-d_4 (0.33 mmol, 15.0 equiv) was condensed into a 4.7-mL bulb containing a degassed solution of **1** (13.9 mg, 0.021 mmol) in C_6D_6 (1.00 mL). After heating to 38 °C for 2.5 h, the solvent was removed under reduced pressure and 13.0 mg of **1**-d_4 was sublimed from the residue (94% yield). This was dissolved in pentane (2 mL) and a second charge of ethylene-d_4 (0.38 mmol, 19.0 equiv) added. Following 3.0 h at 37 °C, the solution was degassed at −76 °C and a third charge of ethylene-d_4 (0.38 mmol, 19.0 equiv) was added. The solution was stirred at 39 °C for 2.3 h. A 2.8-mg sample of this with 0.030 mmol of ethane added as an internal reference showed 4.1% of undeuterated **1** remaining. The benzene was removed under 35 °C, 3 × 10^{-4} Torr.

(*RR,SS*)-(μ-Ethanediyl)octacarbonyldiosmium-*3,4*-d_2, *trans*-1-*3,4*-d_2. *trans*-Ethylene-*1,2*-d_2 (0.66 mmol, 20.0 equiv) was condensed into an 8.1-mL bulb containing a degassed solution of **1** (20.6 mg) in C_6D_6 (1.81 mL). This solution was stirred for 3 h at 40 °C, degassed at −76 °C, and assayed by ^1H NMR ($\delta_1 = 1.51$, $\delta_{1\text{-}d_2} = 1.48$), and a second 0.66-mmol charge of *trans*-ethylene-*1,2*-d_2 was added. Following 2.5 h at 40 °C, a second NMR assay showed 0.25% **1** (relative to *trans*-**1**-*3,4*-d_2). The C_6D_6 was removed, and 12.8 mg (62% yield) of spectroscopically pure[11] *trans*-**1**-*3,4*-d_2 sublimed from the residue (30−35 °C, 3 × 10^{-4} Torr).

(*RS,SR*)-(μ-Ethanediyl)octacarbonyldiosmium-*3,4*-d_2, *cis*-1-*3,4*-d_2. As above, *cis*-ethylene-*1,2*-d_2 (0.72 mmol, 14.7 equiv) was added to a degassed solution of **1** (30.3 mg) in C_6D_6 (1.50 mL). This solution was stirred for 2 h at 37 °C, degassed

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at −76 °C (to remove the ethylene), and assayed by ^1H NMR ($\delta_1 = 1.51$, $\delta_{1\text{-}d_2} = 1.48$). A second 0.73-mmol charge of *cis*-ethylene-*1,2*-d_2 was added, the benzene was removed under reduced pressure after 3.3 h at 37 °C, and *cis*-**1**-*3,4*-d_2 was sublimed from the residue (30−35 °C, 10^{-4} Torr). The sublimate was redissolved in C_6D_6 (1.50 mL); a second NMR assay showed 7.0% of **1** remaining. *cis*-Ethylene-*1,2*-d_2 (0.68 mmol, 13.0 equiv) was added and the solution heated to 37 °C for 3.0 h. A final NMR assay showed 0.5% **1** (relative to *cis*-**1**-*3,4*-d_2). The C_6D_6 was removed, and 13.5 mg (43.5% yield) of spectroscopically pure[11] *cis*-**1**-*3,4*-d_2 sublimed from the residue (30−35 °C, 10^{-4} Torr).

Thermal Exchange Reaction of C_2H_4 with *trans*-1-*3,4*-d_2. *trans*-Ethylene-*1,2*-d_2 (0.12 mmol, 10 equiv) was condensed and sealed in a 5-mm NMR tube containing a solution of **1** (7.7 mg, 0.012 mmol) in CD_2Cl_2 (0.35 mL). After 80 min at 48 °C the contents were transferred to a second tube and degassed at −76 °C. A second aliquot of *trans*-ethylene-*1,2*-d_2 was condensed and sealed into this tube. After heating to 48 °C for 80 min, an NMR assay of the sample ($\delta_1 = 1.61$, $\delta_{1\text{-}d_2} = 1.59$) showed that only a trace of the undeuterated **1** remained. The solution was transferred to a third NMR tube, the CD_2Cl_2 was removed under reduced pressure, fresh CD_2Cl_2 and C_2H_4 were added (0.12 mmol, 10 equiv), and the tube was sealed. This tube was heated to 48 °C for 66 min and cooled to −76 °C, and the volatile materials were passed through a U-tube trap, cooled to −100 °C, into a gas-phase IR cell. Using the procedure described below for *cis*- and *trans*-ethylene-*1,2*-d_2 analysis, the ethylene-d_2's produced were shown to be 98.5 ± 0.3% *trans*-ethylene-*1,2*-d_2.

Ethylene Extrusion from *trans*-1-*3,4*-d_2. Octane (10.0 mL) was added to 11.0 mg of *trans*-**1**-*3,4*-d_2 in a 50-mL Schlenk flask; the flask was attached to a cold finger condenser connected to a high-vacuum line. The octane solution was degassed and the system filled with N_2. A syringe needle was inserted through a septum and stopcock on the sidearm of the Schlenk flask, and its tip was placed in the octane solution. A N_2 flow of 60−70 mL/min went through the solution, past the −76 °C cold finger, and through two U-tube traps and an oil bubbler.

The two U-tube traps were cooled to −196 °C and the octane solution of *trans*-**1**-*3,4*-d_2 was heated to 130 °C for 5 min. The reaction solution, which had become yellow and cloudy, was then cooled to 0 °C. IR analysis showed complete disappearance of the starting material; bands characteristic of $Os_3(CO)_{12}$ and a broad absorption from 2060 to 1933 cm^{-1} were present.

Following the removal of condensed N_2 from the U-tube traps, their contents were transferred to a gas-phase IR cell and analyzed as described below. The ethylenes formed were 99.4 ± 0.3% *trans*-ethylene-*1,2*-d_2.

Ethylene Extrusion from *cis*-1-*3,4*-d_2. Using the same procedure and apparatus as in the thermolysis of *trans*-**1**-*3,4*-d_2 above, 4.1 mg of *cis*-**1**-*3,4*-d_2 (6.0 μmol) in 10.0 mL of octane was heated to 130 °C for 5 min, and the volatile products were transferred to a gas-phase IR cell. The ethylenes present were shown to be 98.8 ± 0.6% *cis*-ethylene-*1,2*-d_2.

Prolonged Exchange of *trans*-1-d_2 with *trans*-HDC=CHD. Upper Limit on Loss of Stereochemistry. (*R,S*)-(*μ*-Ethanediyl)octacarbonyldiosmium-*1,2*-d_2 (**1**-d_2) (4.0 mg) was dissolved in 1 mL of distilled degassed octane and the solution was placed in a side arm attached to a gas IR cell (10-cm path length) equipped with a vacuum-line adapter; the total gas volume of the system was 199 mL. The solution was degassed, 79.0 Torr (1 mmol) of *trans*-ethylene-*1,2*-d_2 was added, and the side arm was placed in a thermostated 40 °C (±0.2 deg) silicone oil bath while the solution was stirred. The apparatus was periodically removed from the bath and an IR spectrum of the gases above the octanes obtained. The initial IR spectrum was taken in the absorbance mode; after 5 days a second IR spectrum was taken in the absorbance mode. Analysis by the procedure described in the next section showed <0.10% *cis*-ethylene-*1,2*-d_2 (1.0×10^{-6} mol).

IR Analysis of *cis*- and *trans*-Ethylene-*1,2*-d_2. The integrated intensities of gas-phase IR bands may be used directly to measure the concentration of sample molecules when the appropriate extinction coefficients are known[32]—and they are available for the normal modes of ethylene and its isotopologues.[12] The relative molar quantities of the *cis* and *trans* isomers of ethylene-d_2 were therefore derived from the experimentally determined (by weight of chart paper) integrated band intensities of the characteristic C−H bending modes (842 and 987 cm^{-1}) for the *cis* and *trans* isomers, respectively)[33] adjusted by the known[12] extinction coefficients ($\Gamma_{cis} = 8531 \pm 213$ and $\Gamma_{trans} = 3740 \pm 49$ cm^2/mol; $\Gamma_{cis}/\Gamma_{trans} = 2.28 \pm 0.09$).

Rate Constant for Exchange of 1 with Free Ethylene under Conditions of Stereochemical Experiment. A solution of **1** (29.2 mg, 4.60×10^{-2} mmol) was dissolved in decane (0.957 mL), placed in the side arm of a gas-phase IR cell (path length 10 cm, internal volume 200 mL), and degassed by several freeze/pump/thaw cycles. The cell was then filled with 79.0 Torr of C_2D_4, and the solution was heated to 40.0 °C with efficient stirring. Infrared spectra were collected by removing the side arm from the constant temperature bath and scanning ten times over the spectral region that contains the absorbance due to the C−H wag of C_2H_4 (949.4 cm^{-1}). The side arm was then replaced in the bath; the timer measuring the time of reaction was halted during the spectrum acquisition.

Upon completion of the experiment, a weighted global average rate constant[13] was calculated from kinetic data at eleven different wavenumbers on the peak at 949.4 cm^{-1} by a computer program described elsewhere.[13,34] The observed rate constant was $1.06(1) \times 10^{-4}$ s^{-1} (r^2 from linear regression of ln $|A_t - A_\infty|$ *vs* time was 0.998); $t_{1/2}$ was thus 109(1) min.

Isomerization of *trans*-Ethylene-*1,2*-d_2 by the Nonvolatile Products of Thermolysis. *trans*-Ethylene-*1,2*-d_2 (0.034 mmol) was added to an 8-mL bulb containing a degassed 4.0-mL aliquot of the solution left after ethylene extrusion at 130 °C from *trans*-**1**-*3,4*-d_2 (above). The solution was heated to 130 °C for 2 h and the gas phase transferred to a suitable IR cell. Bands[12] were observed for the formation of equimolar amounts of both *trans*-ethylene-*1,2*-d_2 and *cis*-ethylene-*1,2*-d_2 along with C_2H_3D and C_2HD_3 (present in concentrations approximately equivalent to the *cis* and *trans* isomers).

Reaction of 1 with C_2H_4 To Form 11. C_2H_4 (0.285 mmol, 26 equiv), neopentane (0.090 mmol), and C_6D_6 (0.35 mL) were condensed and sealed in a 5-mm NMR tube containing 7.0 mg of **1** (0.011 mmol). After the tube had been heated to 44 °C for 3.0 h, ^1H NMR analysis showed no change. Raising the

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[32] (a) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986; p 71. (b) Overend, J. In *Vibrational Intensities in Infrared and Raman Spectroscopy*; Person, W. B., Zerbi, G., Eds.; Elsevier: New York, 1982; Chapter 2.

[33] Pinchas, S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic: New York, 1971; p 85.

[34] Our computer program calculates the weighted global average rate constant, $\bar{k}_{obs}$, by the method

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

where

$$w(k_{obs_i}) = \frac{1}{s_i^2 k_{obs_i}}$$

$$n = \text{number of data points}$$

$$s_i = \text{standard deviation of } k_{obs_i}$$

k_{obs_i} are calculated by linear regression at each wavenumber of ln $|A_t - A_\infty|$ *vs* time, a procedure which also yields the s_i.

temperature to 70 °C for 2.8 h produced a 1:1 mixture of **11** and **1**. Further raising the temperature to 100 °C for 2.0 h gave total conversion to **11**. Integration relative to neopentane as the internal reference indicated a 79% yield. No other products were visible in the ^{1}H NMR.

Thermal Exchange of C_2D_4 with a Mixture of 1 and *trans*-11-d_2. C_2D_4 (0.13 mmol, 16.9 equiv) was condensed into a bulb containing a degassed solution of **1** (4.4 mg, 0.070 mmol) and *trans*-**11**-d_2 (4.9 mg, 0.015 mmol, prepared photochemically from *trans*-ethylene-*1,2*-d_2 and $Os_3(CO)_{12}$ as described below) in 10.0 mL of hexane. The solution was heated at 40–45 °C for 5 h and then cooled to −76 °C; the volatile contents were transferred to a gas-phase IR cell. Comparison of the spectrum with that of the initial atmosphere showed the appearance of a band at 947 cm^{-1}, characteristic of C_2H_4.[12] The bands of *cis*- or *trans*-ethylene-*1,2*-d_2 at 987 and 842 cm^{-1} (see above) were not observed. The IR of the reaction solution showed no change.

Reaction of 11 with C_2D_4, 100 °C. C_2D_4 (0.363 mmol, 20.2 equiv) was transferred in vacuo to a 5-mm NMR tube containing **11** (6.0 mg, 0.018 mmol) and C_6D_6 (0.37 mL). After degassing, the tube was sealed and heated to 44 °C for 3.5 h. NMR analysis showed no evolution of C_2H_4. A trace of C_2H_4 could be detected after 2.5 h at 70 °C, and 2.0 h at 100 °C led to C_2H_4 evolution along with decomposition of **11**.

Photochemical Reaction of *trans*-Ethylene-*1,2*-d_2 with $Os_3(CO)_{12}$. *trans*-Ethylene-*1,2*-d_2 (1.12 mmol, 20 equiv) was condensed into an 8.0-mL bulb with $Os_3(CO)_{12}$ (51 mg, 0.056 mmol) in 5.0 mL of CH_2Cl_2. This heterogeneous mixture was irradiated with the light from a $NaNO_2$-filtered high-pressure quartz mercury-vapor lamp at 25 °C until all the $Os_3(CO)_{12}$ was dissolved to form a straw colored solution (ca. 48 h). IR analysis of the gas mixture over the solution shows ~5% of *cis*-ethylene-*1,2*-d_2 (relative to *trans*). The mononuclear **11**-d_2 was collected in a U-tube cooled to −40 °C on a high-vacuum line and then vacuum transferred to a tared bulb: 17.0 mg, 92% yield. The nonvolatile residue in the photolysis reaction bulb was dissolved in 2 mL of CH_2Cl_2 and eluted from a 2-mm plate on a Chromatotron with pentane. Upon removal of solvent 24 mg of **1**-*3,4*-d_2 was obtained. ^{1}H NMR in the nematic-phase solvent TNC-1565 showed **11** to have the spectrum predicted[11] for **11**-d_2; the spectrum of **1**-*3,4*-d_2 showed no observable contamination by the *cis* isomer.[11]

Photochemical Exchange Reaction of Ethylenes with 1, 0 °C. (a) C_2D_4 (0.18 mmol, 20 equiv) and neopentane (0.030 mmol) were condensed into a 5-mm NMR tube containing a solution of **1** (5.6 mg) in C_6D_6 (0.37 mL); the tube was then sealed. After an initial ^{1}H NMR analysis at 10 °C, the tube was placed in an ice bath and irradiated with a Hanovia high-pressure Hg-vapor lamp filtered with a concentrated (aqueous) $NaNO_2$ solution (λ > 436 nm) for a total of 125 min; NMR showed only a small amount of ethylene evolved. Subsequent exposure to unfiltered irradiation for 38 min at 0 °C led to extensive exchange of C_2D_4 with **1**.

(b) *trans*-Ethylene-*1,2*-d_2 (0.38 mmol, 20.0 equiv) was condensed into a 4.7-mL bulb containing **1** (12.3 mg) in pentane (2.0 mL). This solution was cooled to 0 °C and irradiated for 40 min, the volatiles were remoevd with the solution cooled to −76 °C, and a second charge of *trans*-ethylene-*1,2*-d_2 was added. Following a second irradiation (50 min), the solvent was removed under reduced pressure, the residue was dissolved in 1 mL of CH_2Cl_2, and the solution was filtered through a plug of SiO_2 into a 5-mm NMR tube. The IR spectrum showed peaks exclusively assignable to a diosmacyclobutane. ^{1}H NMR in the nematic-phase solvent TNC-1565 showed a spectrum characteristic[11] of *trans*-**1**-*3,4*-d_2, with no observable contamination by *cis*-**1**-*3,4*-d_2.

Photochemical Exchange Reaction of C_2D_4 with a Mixture of 1 and *trans*-11-d_2. C_2D_4 (0.13 mmol, 16.9 equiv) was condensed into a bulb with a degassed solution containing **1** (4.4 mg, 0.007 mmol) and *trans*-**11**-d_2 (4.9 mg, 0.015 mmol) in 10.0 mL of hexane. The solution was cooled to 0 °C and exposed to the unfiltered radiation of a Hanovia high-pressure Hg-vapor lamp for 5 min. The reaction solution was cooled to −76 °C, and the volatiles were transferred to a gas-phase IR cell. Analysis[12] showed C_2D_4 (719 cm^{-1}) and C_2H_4 (949 cm^{-1}), but no *cis*- or *trans*-ethylene-*1,2*-d_2. The IR cell contents were condensed back into the reaction bulb, cooled to 0 °C, and irradiated for an additional 35 min. IR analysis[12] of the −76 °C volatiles showed the presence of *trans*-ethylene-*1,2*-d_2 (987 cm^{-1}), C_2H_4, C_2D_4, a small amount of C_2D_3H (918 cm^{-1}), and a trace of *cis*-ethylene-*1,2*-d_2 (842 cm^{-1}).

Thermal Reaction of 1 with H_2. A solution of **1** (0.022 mmol) in hexane (10.0 mL) was degassed and transferred to a Fischer-Porter bottle (75 mL) by syringe, cooled to 0 °C, and pressurized with 5.4 atm (80 psi) of H_2. The bottle was then heated to 44 °C for 4 h. The IR assay showed only the bands characteristic of $H_2Os_2(CO)_8$[35] and a trace of **1**.

The solution was transferred to a 50-mL Schlenk flask, and methyl iodide (~1 g) was added. After 12 h at 25 °C the solvent was removed under reduced pressure, leaving 16 mg of a light yellow solid (85% crude yield). IR showed the bands characteristic of $I_2Os_2(CO)_8$[36] and the formation of a small amount of $I_2Os(CO)_4$.

Following the same procedure a solution of **1** was treated with H_2 at 25 °C. The IR assay showed 60% reaction after 48 h, and after 96 h only a trace of **1** remained. The only observable product was $H_2Os_2(CO)_8$.[35]

Photochemical Reaction of 1 with H_2. An atmosphere of H_2 was placed over 3 mL of a 3.2×10^{-2} M solution of **1** in hexane. This was cooled to 0 °C and irradiated for 5 min with the unfiltered radiation of a Hanovia high-pressure Hg-vapor lamp. IR analysis of the resulting solution showed complete consumption of **1** and formation of $H_2Os_2(CO)_8$.[35]

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