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# $\alpha$- versus $\beta$-Hydrogen elimination in the formation of propene from an osmacyclobutane

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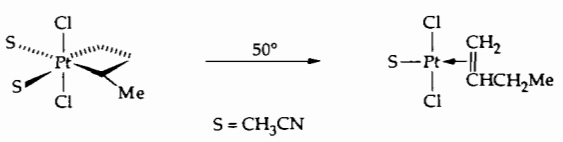
**Abstract**

$Os(CO)_4(CH_2CD_2CH_2)$ has been prepared from $TsOCH_2CD_2CH_2OTs$ and $Na_2[Os(CO)_4]$ and used to investigate the mechanism of propylene extrusion from this osmacyclobutane. Propylene is the principal product whether the thermolysis of the osmacyclobutane is carried out in solution or in a gas phase flow system. Control experiments confirm that the osmacyclobutane does not rearrange prior to thermal decomposition, and that no secondary reactions affect the position of the deuterium labels in the propylene after it is formed in the gas phase. Both $CH_3CD{=}CHD$ and $CH_2DCD{=}CH_2$ are formed, indicating that both $\alpha$- and $\beta$-hydrogen elimination mechanisms are operative. The insertion of CO into the osmacyclobutane ring is facile and may be a step in the propylene extrusion mechanism.

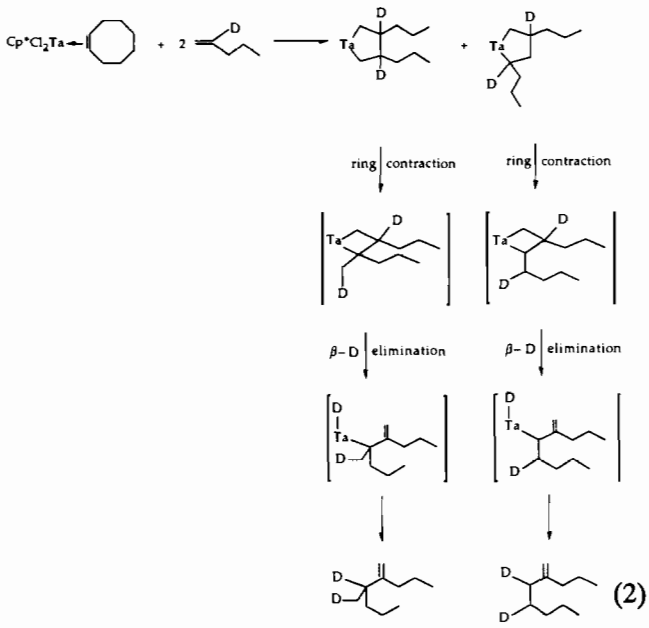
## Introduction

Most metallacycle chemists have assumed that the extrusion of olefins from metallacycloalkanes occurs by a $\beta$-hydrogen elimination mechanism. It is clear, however, that such $\beta$-hydrogen eliminations are more difficult for metallacycloalkanes than for their acyclic counterparts [1]. As the size of metallacycloalkane rings decreases it becomes more difficult for the metal and the $\beta$ hydrogen to achieve the *syn* configuration needed for elimination, so our chances of finding alternative mechanisms of olefin extrusion should increase.

Nevertheless the initial step in metallacyclobutane thermolysis reactions like (1) [2] has traditionally been assumed to be $\beta$-hydrogen elimination. Such a mechanism is necessary to explain the position of the deuterium labels in the products of the ring contraction reaction (2) [3].




(1)




(2)

In fact no metallacyclobutane has ever been *directly observed* to form an allyl hydride complex by $\beta$-hydrogen elimination [4]. An alternative olefin extrusion mechanism starting with $\alpha$-hydrogen elimination (eqn. (3)) has been mentioned as a possibility by Whitesides and co-workers [1b]. The results of the platinacyclobutane rearrangement in eqn. (4) have provided evidence for the $\alpha$-elimination mechanism in eqn. (5) [5].

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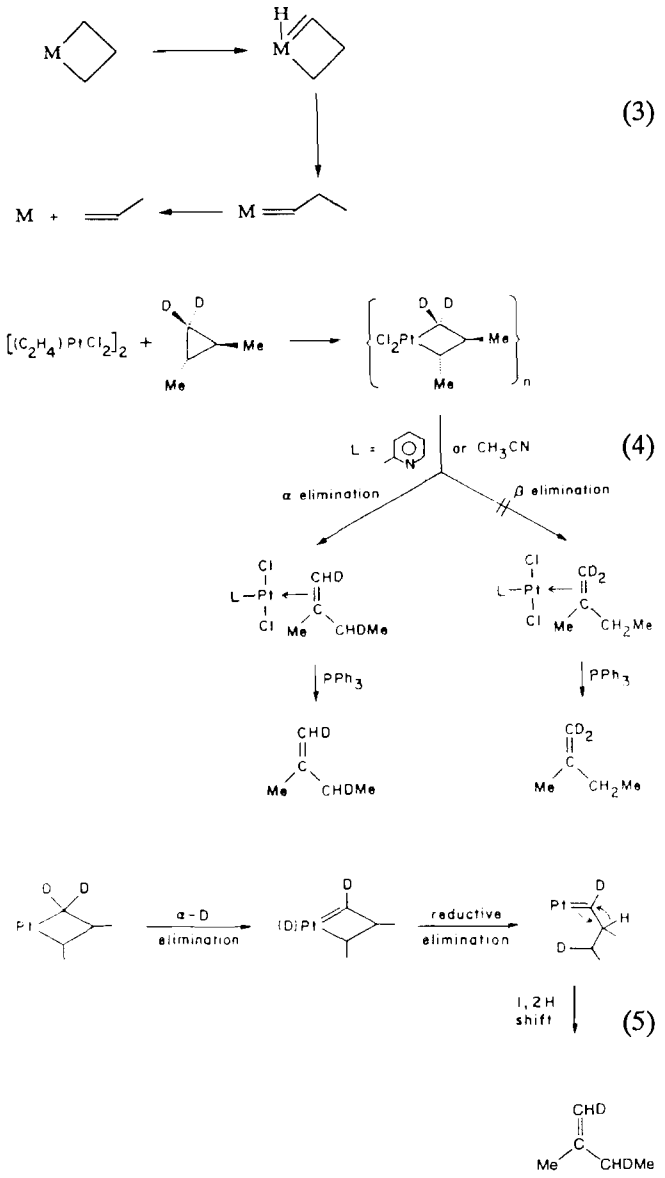


(3)

(4)

(5)

Distinguishing between $\alpha$- and $\beta$-hydrogen elimination mechanisms is difficult in a metallacyclobutane prepared from cyclopropane because any deuterium label in the cyclopropane will be randomly distributed between the $\alpha$ and $\beta$ carbons of the metallacyclobutane. However, we have found it straightforward to prepare an osmacyclobutane from $TsOCH_2CH_2CH_2OTs$ and $Na_2[Os(CO)_4]$. This procedure has made it easy for us to prepare the $\beta,\beta$-dideuterio osmacyclobutane and to investigate whether propylene extrusion from it occurs by $\alpha$- or $\beta$-hydrogen elimination.

## Experimental

Reactions and manipulations were performed under an atmosphere of nitrogen purified by passage through BTS catalyst (BASF) and molecular sieves (3 Å Linde). $Na_2[Os(CO)_4]$ was stored and handled in a nitrogen atmosphere box.

IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. $^1H$ and $^2H$ NMR spectra were recorded on an IBM WP-270-SY or a Bruker AC-300P spectrometer. The isotopic contents of the various propylenes and other organic solvents were determined on a Hewlett-Packard 5988 GC/MS, in a full scanning mode, using a JNW Scientific GSQ column (30 m length, 0.53 inner diameter). The analyses were done by the Central Analytical Laboratory of the Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder.

*$Na_2[Os(CO)_4]$*

This was prepared by a modified version of a previously published method [6]. The $Na/NH_3$ solution was kept under an atmosphere of nitrogen (rather than under its own vapor pressure) and chilled to $-40$ °C; also, more $NH_3(l)$ was used (150 ml with 3 g $Os_3(CO)_{12}$). These modifications significantly decreased the time needed for the reaction while continuing to give a high yield.

$EtO_2CCD_2CO_2Et$ was prepared by exchanging neat diethyl malonate twice with $K_2CO_3/D_2O$; $^1H$ NMR analysis showed 98.9% deuterium incorporation. The alcohol was prepared by reduction with $LiAlH_4$ in THF, and $TsOCH_2CD_2CH_2OTs$ (**2**-2,2-$d_2$) was prepared by treating the alcohol with TsCl and py; pure product was obtained by extraction with boiling $Et_2O$ followed by crystallization at $-23$ °C. $HOCD_2CD_2CD_2OH$ was prepared by reducing $EtO_2CCD_2CO_2Et$ with $LiAlD_4$ instead of $LiAlH_4$, and converted to $TsOCD_2CD_2CD_2OTs$ (**2**-$d_6$) by TsCl/py; $^2H$ NMR ($CDCl_3$) $\delta$ 1.94 (2D), 4.03 (4D).

*$(CO)_4Os(CH_2CH_2CH_2)$ (1)*

**Caution**: thick-walled vessels should be used for all dimethyl ether reactions, in view of the hazard presented by its room temperature vapor pressure. The ditosylate of 1,3-propanediol (130.0 mg, 0.338 mmol) and $Na_2[Os(CO)_4]$ (106.0 mg, 0.304 mmol) were placed in a 25 ml reaction bulb, 5 ml of $Me_2O$ was added by vacuum transfer, and the mixture was degassed. After 24 h at 0 °C, the volatile contents were allowed to distill *in vacuo* through two U-tubes connected in series and cooled to $-76$ and $-196$ °C. After the $-76$ °C trap was evacuated to a pressure $<10^{-4}$ torr, it was allowed to warm to room temperature and 36.3 mg of colorless liquid **1** were vacuum transferred into a tarred bulb. The contents of the $-196$ °C U-tube (largely $Me_2O$) were then returned to the bulb containing the reaction mixture, degassed, and warmed to 0 °C for an additional 38 h. The isolation procedure was repeated

and an additional 40.0 mg of product was vacuum transferred into the tarred bulb (76.3 mg total, 73% yield). Spectroscopic data agreed with those reported by Lindner *et al.* [7]. IR (pentane): 2121 (w), 2038.3 (sh), 2034.4 (s), 2005.3 (s). $^1$H NMR ($C_6D_6$): $\delta$ 3.74 (quintet, $J$=7.9, 2H), 0.64 (t, $J$=7.9 Hz, 4H); ($CD_2Cl_2$: $\delta$ 3.71, 0.68. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 39.4 ($J$(CH)=125.0 Hz), −37.5 ($J$(CH)=137.7 Hz).

*1-$d_6$*

$Na_2Os(CO)_4$ (220 mg, 0.64 mmol) was added to $TsOCD_2CD_2CD_2OTs$ (273 mg, 0.7 mmol) in a thick-walled high-pressure Schlenk flask. 8 ml $Me_2O$ were added to the flask, and the mixture was stirred under vacuum at 25 °C for 2 days. The solvent was removed at −78 °C and the flask allowed to warm to 25 °C. Pure product was collected as in the previous section, in a trap at −78 °C (33% yield). $^2$H NMR ($C_6D_6$): $\delta$ 0.54 (4D), 3.61 (2D). **1**-3,3-$d_2$ was similarly prepared from **2**-2,2-$d_2$.

*The osmacyclopentane 5*

This was prepared from $TfOCH_2CH_2CH_2CH_2OTf$ and $Na_2[Os(CO)_4]$ in $Me_2O$ as reported by Lindner *et al.* [7]. In $C_6D_6$ its $^1$H NMR spectrum showed peaks at $\delta$ 1.70 and $\delta$ 1.56.

*The osmacyclopentanone 3*

The osmacyclobutane **1** (41.0 mg, 0.119 mmol) and 5 ml THF were vacuum transferred into a 25 ml bulb and placed under 640 torr of CO. After 5.5 h at 77 °C, the THF was removed under reduced pressure and the residue extracted with 10 ml of pentane. This was filtered, reduced to ~3 ml, and cooled to −76 °C. A white solid precipitated after 15 min and the mother liquor was removed to yield 33.2 mg of **3** (75%). IR (pentane): $\nu$(CO)=2126 (w), 2056 (m), 2037 (s), 2028 (s), 2004 (w) cm$^{-1}$; $\nu$(acyl)=1670 cm$^{-1}$. $^1$H NMR ($C_6D_6$): $\delta$ 1.93 (t, $J$=6.7 Hz, 2H), 1.80 (m, 2H), 1.75 (t, $J$=7.0 Hz, 2H). The mass spectrum showed a parent ion at $m/e$ 374 ($^{192}$Os) with an isotope pattern in agreement with that calculated for $OsC_8H_6O_5$.

*Carbonylation of 1, 4 and 5*

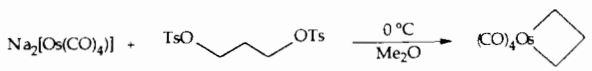
Solutions of **4, 1** (4.2 mg, 1.2 $\mu$mol) and **5** in $CD_2Cl_2$ (0.44 ml total volume) were placed in a 5 mm NMR tube, degassed and sealed under ~640 torr of CO. NMR integration showed the molar ratio of **4:1:5** = 1.0:2.5:1.8. After 19.3 h at 45 °C very little change had occurred. Further heating at 63 °C for 24 h led to the complete consumption of **1** to form **3**. The diethyl complex **4** was slowly converted to a mixture of compounds over a period of 116 h at 65 °C. The amount of **5** (relative to $CHDCl_2$) remained constant throughout the thermal treatment.

*General procedure for thermal decomposition in gas phase flow system*

A flask containing the osmacycle was connected to a pyrolysis tube (filled with glass beads and wrapped with a heating tape) and two U-tubes attached to a high-vacuum system. The whole system was evacuated to $<10^{-5}$ torr and the tube heated to 300 °C. The osmacycle was allowed to sublime slowly through the preheated pyrolysis tube and the products were collected at −196 °C in the U-tubes.

## Results and discussion

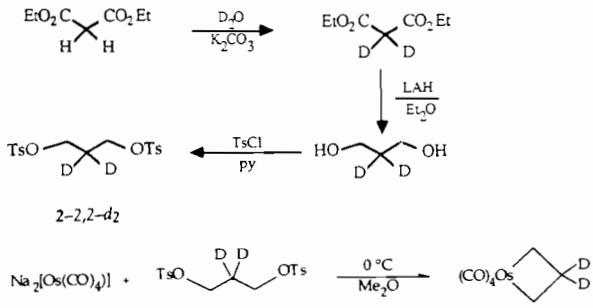
The low boiling point (−24.8 °C) and high vapor pressure (23 mm Hg at −45 °C) of dimethyl ether make it useful as a solvent for the reaction of $Na_2[Os(CO)_4]$ with electrophiles [6]. Volatile products such as the osmacyclobutane **1** can be isolated in good yield after a suspension of $Na_2[Os(CO)_4]$ in $Me_2O$ is treated with $TsOCH_2CH_2CH_2OTs$ (eqn. (6)). (The preparation of **1** in 46% yield from $Na_2[Os(CO)_4]$ and the corresponding ditriflate in $Me_2O$ has been reported by Lindner *et al.* [7].)




(6)

**1** (77% yield)

Deuterated derivatives of $TsOCH_2CH_2CH_2OTs$ are easily prepared. Diethyl malonate can be deuterated by exchange (eqn. (7)), and reduction and tosylation to give **2**-2,2-$d_2$. Use of the latter in eqn. (8) provided the deuterated osmacyclobutane **1**-3,3-$d_2$.



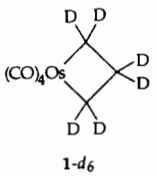

(7)

2-2,2-$d_2$




(8)

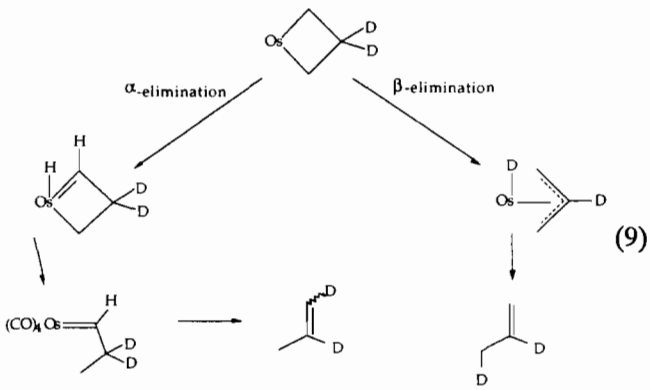
Use of $LiAlD_4$ in eqn. (7) gave **2**-$d_6$ and eventually **1**-$d_6$.




1-$d_6$

Thermal decomposition of **1** gives propylene under virtually all conditions. (We have found no evidence

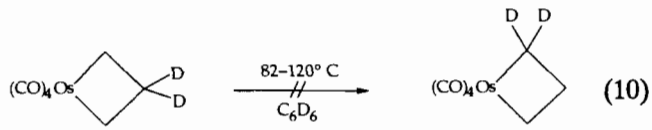
for the cyclopropane reported by Lindner *et al.* [7] as the product of the thermolysis of **1**.) In principle (see eqn. (9)) the use of **1**-3,3-$d_2$ should make an $\alpha$-hydrogen elimination mechanism like eqn. (3) readily distinguishable from a $\beta$-hydrogen elimination mechanism.



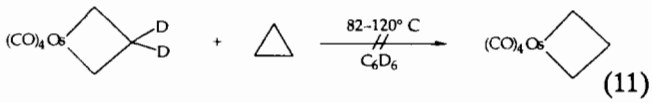

(9)

However, such experiments require that we examine the primary product of the reaction. In order to write a detailed mechanism we must also know of any rearrangements in **1** prior to propene elimination.

We began by examining the thermal decomposition of **1** in solution. A solution of **1**-3,3-$d_2$ showed no rearrangement of deuterium from the $\beta$ to the $\alpha$ position when heated to 120 °C (eqn. (10)), ruling out any mechanism (i.e. reversible formation of a cyclopropane intermediate) in which the three carbons became equivalent prior to elimination. Furthermore, no cyclopropane was incorporated back into **1** under the conditions of eqn. (11); the cyclopropane remained unchanged.

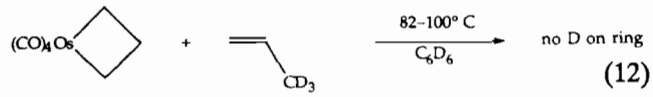



(10)

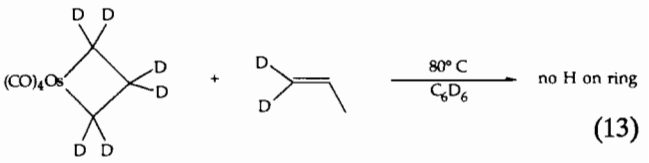



(11)

Similar experiments showed that propylene was not incorporated back into **1**. For example, $^2$H NMR showed that no deuterium was incorporated into **1** under the conditions of eqn. (12), and $^1$H NMR showed that no $^1$H was incorporated into **1** under the conditions of eqn. (13). However, these experiments also showed that a secondary reaction was scrambling deuterium labels within propylene. For example, during reaction (13) signals appeared in the $^2$H NMR spectrum indicating migration of D from C-1 of the propylene to C-2 and C-3.

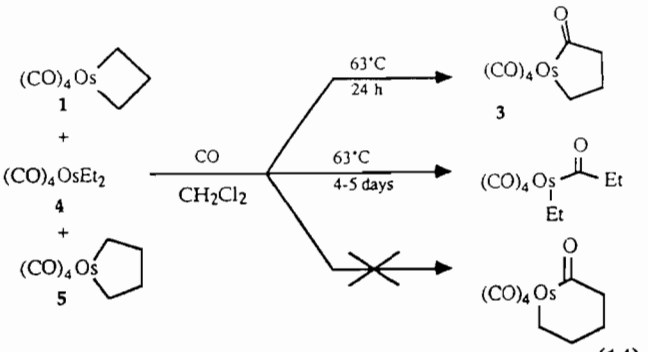



(12)




(13)

Finally, these experiments revealed that large amounts of an acyl osmium species were formed prior to propylene elimination – an observation that prompted us to investigate the carbonylation of **1**. Under 640 torr CO the osmacyclobutane **1** was easily carbonylated to the acyl **3** (5.5 h, 77 °C, THF). The effect of ring strain on ease of carbonylation was briefly investigated by comparing the behavior toward CO of **1**, the acyclic diethyl complex **4** [6] and the osmacyclopentane **5** (easily prepared from $Na_2[Os(CO)_4]$ and $TfOCH_2CH_2CH_2CH_2OTf$ in $Me_2O$ [7]). A mixture of **1**, **4** and **5** under CO gave the results in eqn. (14); **1** was completely converted to **3** before significant carbonylation of **4** occurred, whereas the osmacyclopentane **5** did not react. The osmacyclobutane **1** is clearly strained enough to activate it toward CO insertion relative to the acyclic **4**, whereas the osmacyclopentane **5** is not.




(14)

The osmacyclopentanone **3** was identified among the products when solutions of **1** were heated in sealed tubes in the absence of added CO. After 5 h at 82 °C, $^1$H NMR showed that 70% of the **1** in a $C_6D_6$ solution had been converted into **3**; propylene formation was considerably slower (days at 120 °C).

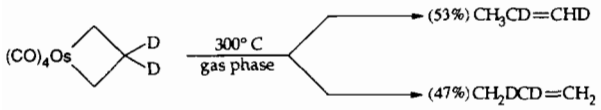
*Direct observation of thermal decomposition products*

In order to preclude secondary reactions we attempted to remove propylene from these reactions as rapidly as it was formed. We obtained some propene-$d_1$ and propene-$d_3$ from the thermolysis of a mineral oil solution of **1**-3,3-$d_2$ under a vacuum. This result required an intermolecular mechanism of some kind and suggested that secondary reactions were still occurring after the propylene had been formed.

We therefore examined the thermolysis of **1** in a gas phase flow system at 300 °C. Under these conditions

an 86% yield of propylene was obtained from **1**. GC/MS showed *only* propene-$d_2$ from the labelled osmacyclobutane **1**-3,3-$d_2$, i.e. there were no intermolecular products and no secondary reactions. Control experiments with $CD_3CH{=}CH_2$ confirmed that our flow system at 300 °C did not affect the label distribution within propylene; other control experiments showed that cyclopropane did not rearrange to propylene under these conditions.

$^1$H NMR analysis of the propene-$d_2$ formed by the thermolysis of **1**-3,3-$d_2$ showed no H on C-2*. The only products were thus $CH_3CD{=}CHD$ (the product of the $\alpha$-elimination mechanism in eqn. (9)) and $CH_2DCD{=}CH_2$ (the product of the $\beta$-elimination mechanism in eqn. (9)). The observed methyl/vinyl $^1$H NMR ratio of 1.73 implied a 53% yield of $CH_3CD{=}CHD$ and a 47% yield of $CH_2DCD{=}CH_2$ as the primary products of the gas phase thermolysis of **1**-3,3-$d_2$ (eqn. (15)).

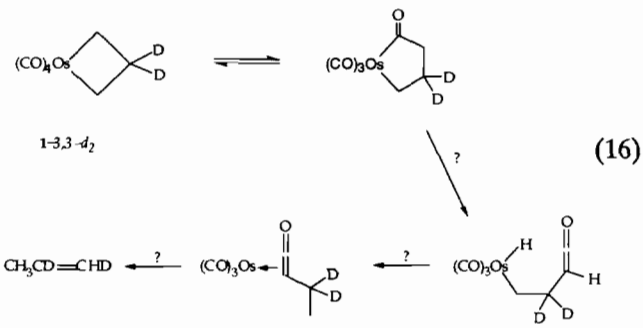



(15)

We conclude that (i) some of the propylene from the osmacyclobutane **1** is indeed formed by $\alpha$-hydrogen elimination, but that (ii) both $\alpha$- and $\beta$-elimination mechanisms occur. The relative yields of $CH_3CD{=}CHD$ and $CH_2DCD{=}CH_2$ imply that, per H or D, a $\beta$ deuterium is about twice as likely to be eliminated by the metal than an $\alpha$ hydrogen. Any mechanism involving a symmetric intermediate with all carbons equivalents is unlikely (an inverse kinetic isotope effect of two is improbable at that temperature).

However, the ease with which acyls can be formed from **1** in solution suggests that we ought to consider mechanisms involving acyl intermediates like the one in eqn. (16). The increase in ring size after CO insertion may make $\beta$-deuterium elimination easier, and one pair of $\alpha$ hydrogens in **1** have become $\beta$ hydrogens in **6**; their elimination, and the intermediate formation of a ketene complex [8–10], offer an alternative route to $CH_3CD{=}CHD$.

*There is thus no scrambling of label onto the C-2 of propylene under the conditions of osmacyclobutane thermolysis – even if osmium metal is present from a previous thermolysis.

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**References**

1 (a) J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc., 95* (1973) 4451; (b) *98* (1976) 6521; (c) T. M. Miller and G. M. Whitesides, *Organometallics, 5* (1986) 1473.
2 R. J. Al-Essa, R. J. Puddephatt, D. C. L. Perkins, M. C. Rendle and C. F. H. Tipper, *J. Chem. Soc., Dalton Trans.*, (1981) 1738.
3 (a) S. J. McLain, J. Sancho and R. R. Schrock, *J. Am. Chem. Soc., 102* (1980) 5610, and refs. therein; (b) S. M. Rocklage, J. D. Fellmann, G. A. Ruppert, L. W. Messerle and R. R. Schrock, *J. Am. Chem. Soc., 103* (1981) 1440, and refs. therein.
4 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, California, 1987, Section 9.1d, pp. 469–474.
5 R. J. Puddephatt, in M. H. Chisholm (ed.), *Inorganic Chemistry: Toward the 21st Century*, ACS Symposium Series 211, American Chemical Society, Washington, DC, 1983, pp. 353–366, and refs. therein; J. T. Burton and R. J. Puddephatt, *Organometallics, 5* (1986) 1312.
6 W. J. Carter, J. W. Kelland, S. J. Okrasinski, K. E. Warner and J. R. Norton, *Inorg. Chem., 21* (1982) 3955, and refs. therein.
7 E. Lindner, R.-M. Jansen, W. Hiller and R. Fawzi, *Chem. Ber., 122* (1989) 1403.
8 (a) S. I. Hommeltoft and M. C. Baird, *J. Am. Chem. Soc., 107* (1985) 2548; *Organometallics, 5* (1986) 190; (b) S. Sunch and M. C. Baird, *J. Organomet. Chem., 338* (1988) 255.
9 S. E. Halfon, M. C. Fermin and J. W. Bruno, *J. Am. Chem. Soc., 111* (1989) 5490.
10 G. L. Geoffroy and S. L. Bassner, *Adv. Organomet. Chem., 28* (1988) 1–83.