[OsH$_4$(PPh$_3$)$_3$]: NEW CATALYST FOR THE SELECTIVE CYCLOPROPANATION OF ACTIVATED OLEFINS

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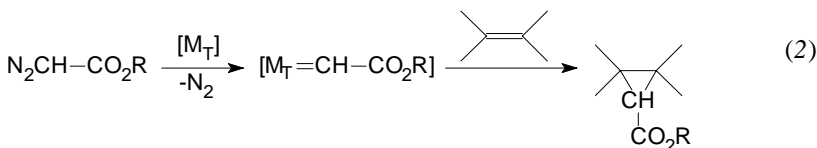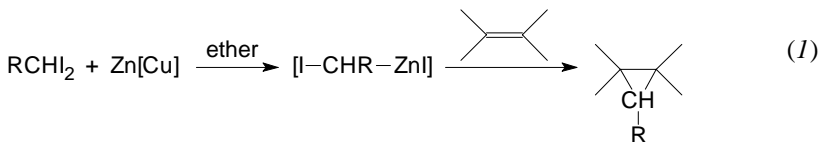
The title compound was found to be an efficient catalyst for the selective cyclopropanation of activated olefins by ethyl diazoacetate. The cyclopropane yields range from moderate to good (75 to 95%) for activated olefins such as styrene and styrene derivatives, but are rather low (20 to 30%) for non-activated olefins such as terminal and cyclic alkenes. In the intermolecular competition, styrene was 45 times more reactive than cyclooctene. In all cases, *trans* (*exo*) cyclopropane predominated over the *cis* (*endo*) isomer.

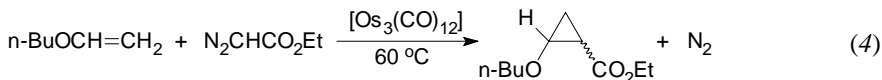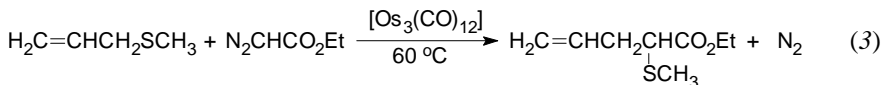**Key words:** Olefins; Diazo compounds; Cyclopropanation; Osmium; Catalysis.

Homogeneous catalysis by platinum metal complexes has been traditionally based on the use of ruthenium, rhodium and palladium[1]. The fact that 5d metals usually form stronger bonds than their 3d and 4d congeners with hydride, olefin, alkyl, phosphine, and other ligands commonly participating in catalytic transformations, has led to the general assumption that reactions typically involving catalytic cycles, such as Lewis base addition–elimination, oxidative addition–reductive elimination, insertion–deinsertion, etc., are too slow for third row metal complexes to be of any practical application in catalysis. However, in the past few years, a number of interesting examples of organic transformations catalyzed by third row metal complexes have been reported in the literature[2].

Most of the studies of osmium-catalyzed reactions performed so far have concentrated on simple model substrates, for instance in the isomerization and hydrogenation of terminal and internal carbon–carbon double and triple bonds and in the reduction of saturated and unsaturated carbonyl compounds. Olefin hydroformylation has also been reported[3,6]. The decisive breakthrough in osmium catalysis so far, however, has been made in the asymmetric dihydroxylation of prochiral olefins using cinchona alkaloid derivatives as the chiral ligands[7,8].

Currently, cyclopropanes hold a prominent position in organic chemistry, both in biologically active compounds and as valuable synthons in organic synthesis. Numerous methodologies have been developed for their construction. Among them, the Simmons–Smith reaction (Eq. (*1*)) and the catalytic cyclopropanation of olefins by diazo compounds (Eq. (*2*)) have emerged as most versatile synthetic reaction pathways.

$$RCHI_2 + Zn[Cu] \xrightarrow{\text{ether}} [I-CHR-ZnI] \longrightarrow \quad (1)$$

$$N_2CH-CO_2R \xrightarrow[-N_2]{[M_T]} [M_T=CH-CO_2R] \longrightarrow \quad (2)$$

Historically, copper-based catalysts have played a prominent role in the in situ generation of metal carbenes from diazo compounds. In the 1970s, new transition-metal complex catalysts were discovered that widened the range of catalytic applications of diazo compounds proceeding under much milder reaction conditions[9–11]. Among those, palladium(II) and copper(I) complexes of poorly coordinating ligands, dirhodium(II) tetracarboxylates and, later, also carboxamides proved to be the most effective. Ruthenium complexes have recently been introduced as cyclopropanation catalysts[11–17] but none of them has been demonstrated to be really superior to rhodium-based catalysts: most of the catalysts often lack stereoselectivity. This justifies the search for alternative catalysts. In this context, osmium-based catalysts, although still poorly documented, look rather attractive. While dodecacarbonyltriosmium [$Os_3(CO)_{12}$] has been reported[18] to exhibit a low activity in the catalytic ylide transformation of allyl methyl sulfide (Eq. (*3*), 4% yield) and cyclopropanation of n-butyl vinyl ether (Eq. (*4*), 13% yield) with ethyl diazoacetate, osmium porphyrins proved to be effective catalysts for the cyclopropanation of alkenes with diazoalkanes.

$$H_2C=CHCH_2SCH_3 + N_2CHCO_2Et \xrightarrow[60\ ^\circ C]{[Os_3(CO)_{12}]} H_2C=CHCH_2\underset{SCH_3}{CHCO_2Et} + N_2 \quad (3)$$

$$n\text{-BuOCH}=CH_2 + N_2CHCO_2Et \xrightarrow[60\ ^\circ C]{[Os_3(CO)_{12}]} \quad + N_2 \quad (4)$$

For instance, $[Os(TTP)]_2$ (TTP = *meso*-tetra-*p*-tolylporphyrinato)[19] led to high yields (up to 80%) and displayed the highest *trans* stereoselectivity (*trans/cis* isomer ratio = 10) in the cyclopropanation of styrene by ethyl diazoacetate[19]. We have recently started studies in this field and, subsequent to our initial reports on the use of $[OsCl_2(PPh_3)_3]$ (ref.[20]) and $[OsCl_2(p\text{-cymene})]_2$ (ref.[21]) (*p*-cymene = 4-isopropyltoluene) as catalysts for olefin cyclopropanation, we turned our attention to $[OsH_4(PPh_3)_3]$ (ref.[22]). In the present paper we report on our preliminary results concerning the use of $[OsH_4(PPh_3)_3]$ as a catalyst for the cyclopropanation of various olefins by ethyl diazoacetate (Eq. (5)) (Table I).

$$R\diagup\!\!= + \; N_2CH-CO_2Et \xrightarrow{[OsH_4(PPh_3)_3]} \underset{cis}{\overset{R \quad CO_2Et}{\diagup\!\!\!\diagdown C_H}} + \underset{trans}{\overset{R \quad H}{\diagup\!\!\!\diagdown C_{CO_2Et}}} \quad (5)$$
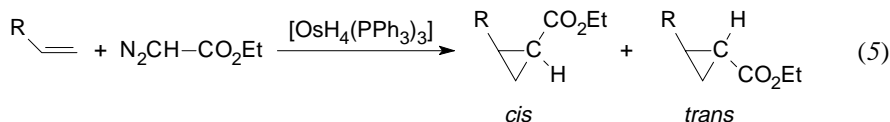
TABLE I
Cyclopropanation yields and stereoselectivities from reactions of ethyl diazoacetate with representative olefins in the presence of $[OsH_4(PPh_3)_3]$

Olefin	Yield, %	*Cis/trans* or *endo/exo* ratio
Styrene, 60 °C (24 h)	40	0.40
Styrene, 80 °C (24 h)	73	0.45
Styrene, 100 °C (8 h)	91 (94)[a]	0.48 (0.51)[a]
4-Methylstyrene	89 (91)[a]	0.46 (0.49)[a]
4-*t*-Butylstyrene	86	0.55
4-Methoxystyrene	90	0.54
4-Chlorostyrene	91 (89)[a]	0.41 (0.46)[a]
4-Bromostyrene	82	0.48
α-Methylstyrene	85	0.62
1,3-Diisopropenylbenzene	87	0.76
Divinylbenzene	89	–
1,2-Dihydronaphthalene[b]	82	0.38
Cyclooctene, 60 °C (70 h)	21	0.57
Cyclooctene, 100 °C (12 h)	29	0.21
1-Octene[b]	19	0.64
1-Decene[b]	23	0.58
1-Dodecene[b]	21	0.50

[a] The reactions were carried out in air, or under nitrogen (results into brackets) with reagents distilled in a vacuum, and kept under nitrogen. [b] With $Rh_2(OAc)_4$: yield 95–100%; *endo/exo* ratio = 0.60 with 1,2-dihydronaphthalene; *cis/trans* ratio = 0.70–0.72 with 1-octene, 1-decene and 1-dodecene.

EXPERIMENTAL

Materials

Ethyl diazoacetate and olefins were purchased from Janssen Chimica and Aldrich and used as received. All olefins were pure reagents, except for divinylbenzene which was purchased as a mixture of isomers (technical purity, 80%, Aldrich, 41,456-5). For some experiments, styrene, 4-methylstyrene, and 4-chlorostyrene were passed through a short column of alumina, distilled in a vacuum and kept under nitrogen. [OsH$_4$(PPh$_3$)$_3$] was synthesized following ref.[22].

Cyclopropanation Reactions

In a typical experiment, [OsH$_4$(PPh$_3$)$_3$] (0.005 mmol) and the olefin (20 mmol) were placed into a round-bottom flask and heated to 100 °C. One ml of a solution of ethyl diazoacetate in the olefin (1 mol l^{-1}) was added dropwise over 4 h to the vigorously stirred system. The stirred reaction mixture was heated at 100 °C for another 4 h and analysed by gas chromatography. The retention times of the cyclopropane products were determined by comparison with authentic samples. The yields were based on ethyl diazoacetate, using dibutyl fumarate or diethyl phthalate as internal GC standards.

RESULTS AND DISCUSSION

Slow (4 h) addition of a styrene solution of ethyl diazoacetate to a vigorously stirred solution of [OsH$_4$(PPh$_3$)$_3$] in styrene at 100 °C resulted in the formation of ethyl 2-phenyl-1-cyclopropanecarboxylate in a 91% yield, as determined by GC. The *cis/trans* isomer ratio was 0.48. Other styrene derivatives were also cyclopropanated by ethyl diazoacetate in the presence of [OsH$_4$(PPh$_3$)$_3$]. The yields were generally high (80–95% based on ethyl diazoacetate). In all examples shown in Table I, the stereoselectivities (*cis/trans* isomer ratios) agreed well with those reported for typical copper-, rhodium-, and ruthenium-based catalysts: the *trans* isomer predominated substantially over the *cis* isomer.
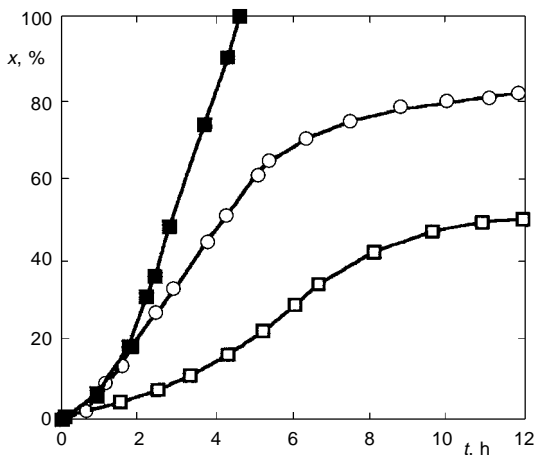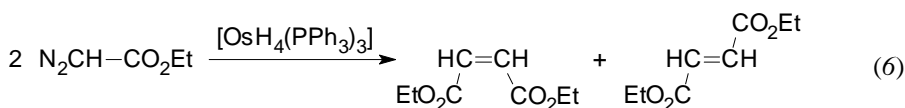

Fig. 1

Nitrogen evolution (x, %) versus time for decomposition of ethyl diazoacetate by [OsH$_4$(PPh$_3$)$_3$] in neat styrene at 60 (□), 80 (○), and 100 (■) °C. Reactions carried out in air

Two features are typical of the cyclopropanation of olefins catalyzed by $[OsH_4(PPh_3)_3]$. First, as shown in Figs 1 and 2, the temperature has a dramatic effect on the ethyl diazoacetate decomposition rate. At 60 °C, a fraction of the diazo compound remained undecomposed even after one day, as confirmed by IR spectroscopy ($\nu(N_2) = 2\ 111\ cm^{-1}$). On the other hand, a short induction period was observed for the decomposition of ethyl diazoacetate in air (Fig. 3) but not under nitrogen if reagents distilled and kept under nitrogen were used (Figs 3 and 4). Second, activated olefins were much more reactive than non-activated olefins (Table I and Fig. 2). This was clearly demonstrated by intermolecular competitions between styrene and cyclooctene. Styrene was 45 times more reactive than cyclooctene at 80 °C (18 times at 60 °C). Such a high selectivity is unmet with classical copper- and rhodium-based catalysts and should lead to fine applications in organic synthesis.

Carbene dimers represented the major by-products emerging from these reactions (Eq. (6)). Diethyl maleate mostly prevailed over diethyl fumarate.

$$2\ N_2CH-CO_2Et \xrightarrow{[OsH_4(PPh_3)_3]} \underset{EtO_2C \quad CO_2Et}{HC=CH} + \underset{EtO_2C}{HC=CH}^{CO_2Et} \tag{6}$$

Polystyrenes were also produced to some extent (polystyrene yield, 15–35%; M_n, 75 000–130 000; M_w/M_n, 1.75–2.0). On the other hand, no metathesis was observed with styrene(s) or cyclooctene, whereas with norbornene, which is a strained cyclo-olefin, no cyclopropanation occurred but instead, polymers were obtained via ring-opening metathesis (Eq. (7)) (polymer yield, 55–75%; M_n, 180 000–350 000; M_w/M_n, 1.75–2.75; *cis/trans* ratio 1.9).
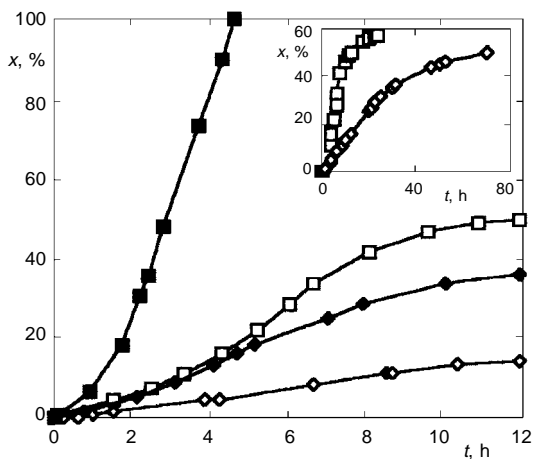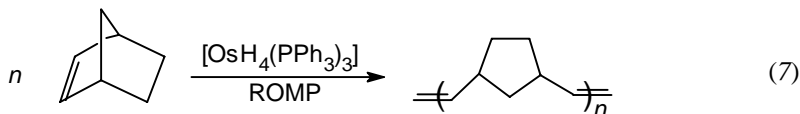

Fig. 2

Nitrogen evolution (x, %) versus time for decomposition of ethyl diazoacetate by $[OsH_4(PPh_3)_3]$ in neat styrene (□, ■) and cyclooctene (◇, ◆), at 60 (□, ◇) and 100 (■, ◆) °C. Reactions carried out in air

$$n \quad \text{[bicyclic alkene]} \quad \xrightarrow[\text{ROMP}]{\text{[OsH}_4\text{(PPh}_3\text{)}_3\text{]}} \quad \text{[polymer]}_n \qquad (7)$$

We presume that the active intermediate is an osmium carbene species formed by reaction of $[OsH_4(PPh_3)_3]$ with ethyl diazoacetate. Under these conditions, one ligand should probably be released from $[OsH_4(PPh_3)_3]$. However, the ^{31}P NMR spectrum of two reaction mixtures (cyclopropanation of 1-octene and 1-dodecene, Table I) displayed the same absorption (δ 28.8) as the pure $[OsH_4(PPh_3)_3]$ complex (free PPh_3 absorbed at δ –5.1 in $CDCl_3$).
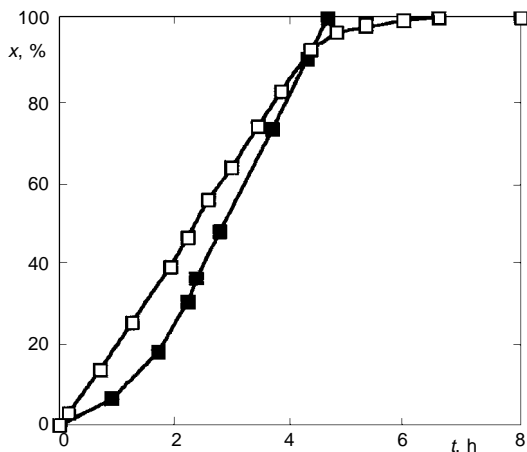

Fig. 3
Nitrogen evolution (x, %) versus time for decomposition of ethyl diazoacetate by $[OsH_4(PPh_3)_3]$ in neat styrene in air ($\blacksquare$) and under nitrogen ($\square$), at 100 °C
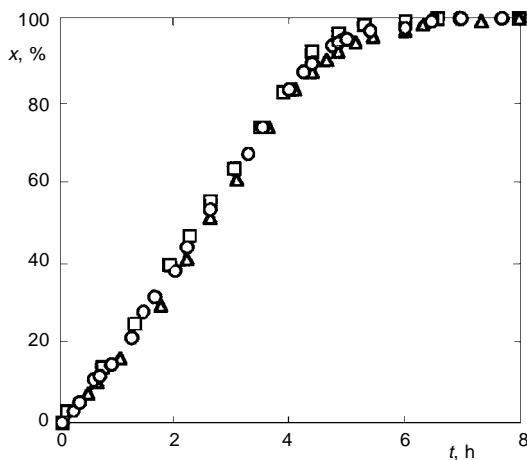

Fig. 4
Nitrogen evolution (x, %) versus time for decomposition of ethyl diazoacetate by $[OsH_4(PPh_3)_3]$ in neat styrene ($\square$), 4-methylstyrene ($\triangle$) and 4-chlorostyrene ($\bigcirc$), in nitrogen at 100 °C

In conclusion, $[OsH_4(PPh_3)_3]$ is an efficient catalyst for the selective cyclopropanation of activated olefins. More detailed studies are now needed to assess its place in the ever-expanding sphere of carbene chemistry.

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