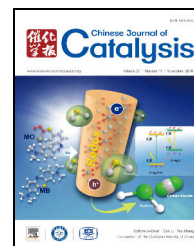


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Review

Osmium complexes in catalysis of olefin hydrogenation and isomerization

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ABSTRACT

This review focuses on the evolution of the use of osmium complexes as catalysts in the hydrogenation and isomerization of olefins. Osmium systems show good catalytic activities and selectivities in the hydrogenation of olefins via both dihydrogen and transfer hydrogenation. Such systems therefore have significant potential to become a powerful tool in organic synthesis.

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1. Introduction

The properties of osmium(II) complexes are similar to those of ruthenium(II) complexes and they can often be prepared using similar methods [1]. In a review of the use of osmium complexes in homogeneous catalysis [2], Sanchez-Delgado and coworkers pointed out that because of the stronger bonding of this 5d metal compared with that of its 4d counterpart, i.e., ruthenium, osmium-based catalysts have higher thermal and oxidative stabilities and therefore slower exchange kinetics for ligands typically involved in catalytic transformations. These factors have led to the general assumption that in the case of osmium the reactions involved in catalytic cycles, such as Lewis base addition–elimination and insertion–deinsertion, are too slow to be attractive for catalytic applications. These authors also suggested that this drawback could be overcome by choosing an appropriate ligand–metal system. This has recently

been confirmed by the development of various osmium-based catalysts that show high performance and versatility in various processes and have efficiencies comparable or superior to those reported for similar ruthenium systems [3,4]; this compensates for the higher costs of osmium precursors compared with those of their analogs. However, despite the considerable progress that has been made in osmium-catalyzed reactions, their use in the hydrogenation and isomerization of alkenes has been neglected. In this review, we outline the evolution of the use of osmium complexes as catalysts in the hydrogenation and isomerization of alkenes, to stimulate research in this field.

2. Mononuclear complexes

The investigation of osmium hydrogenation catalysts began in 1965, when Vaska [5] reported preliminary observations on factors responsible for the catalytic hydrogenation of unsatu-

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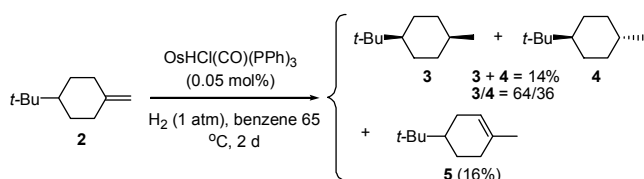
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rated molecules with metal complexes. It was reported that the octahedral hydride d^6 -osmium complex $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ (**1**) catalyzes the hydrogenation of acetylene to ethylene and ethane. Experiments failed to detect hydrogen uptake by this complex (40 °C, 0.92 atm of H_2); it reacted with molecular deuterium to give the corresponding monodeuteride, $\text{OsDCl}(\text{CO})(\text{PPh}_3)_3$, but not the dideuteride, $\text{OsD}_2(\text{CO})(\text{PPh}_3)_3$.

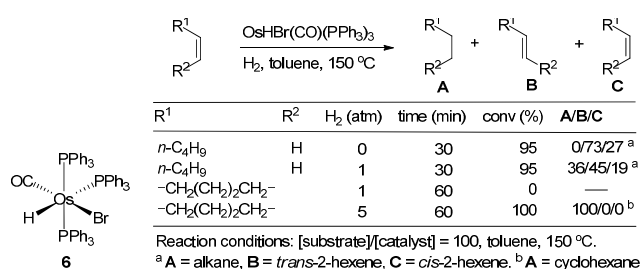
Five years later, the Vaska osmium complex and a number of other metal complexes were assessed for the selective catalytic hydrogenation of 4-*t*-butylmethylenecyclohexane (**2**) [6]. After 2 d at 85 °C under 1 atm of H_2 , **1** (0.05 mol%) gave a mixture of *cis*- (**3**) and *trans*-4-*t*-butylmethylcyclohexane (**4**) (**3**:**4** = 64:36, **3** + **4** = 14% yield) containing the isomerized alkene, 4-*tert*-butyl-1-methylcyclohex-1-ene (**5**) in 16% yield (Scheme 1).

Shortly afterwards, a number of hydrido osmium complexes were prepared and assessed as catalysts in olefin hydrogenation and isomerization [7]. Reaction of the tetrahydride osmium complex $\text{OsH}_4(\text{PEtPh}_2)_3$ in the absence of H_2 with 4 equiv. of cycloocta-1,5-diene in toluene at 100 °C for 65 h gave a 50% yield of cyclooctene and unreacted cyclooctadiene. The reaction of 12 equiv. of oct-1-ene under the same reaction conditions produced various octanes and 2 equiv. of octane. The same complex converted oct-1-ene under 1 atm of H_2 in boiling toluene to octane and a large amount of isomerized products. The complex *cis*- $\text{OsH}_2(\text{PEtPh}_2)_4$ isomerized and hydrogenated oct-1-ene, indicating that more than two atoms of hydrogen per osmium atom are transferred to octane. This complex also catalyzed hydrogenation under H_2 , but the isomerization was much more rapid. Finally, $\text{OsH}_2(\text{CO})(\text{PEtPh}_2)_3$ isomerized octenes in boiling toluene without the formation of octane; the isomerization of oct-2-ene was much slower than that of oct-1-ene. This complex gave only traces of hydrogenation products under H_2 ; the rate of isomerization was similar to that without H_2 .

In a preliminary communication, Sánchez-Delgado and coworkers [8] described the use of the stable mononuclear osmium(II) complex $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$ (**6**; Scheme 2), which was first synthesized by Vaska [9] in 1964 via the reaction of $[\text{OsBr}_6]^{2-}$ with PPh_3 in refluxing 2-methoxyethanol, as a catalyst in various organic transformations, including alkene isomerization and hydrogenation reactions. Under an inert atmosphere, hex-1-ene was rapidly isomerized (30 min) by **6** ([substrate]:[catalyst] = 100:1) in toluene at 150 °C, giving an equilibrium mixture of hex-2-enes; no C=C bond migration to the 3-position was observed (Scheme 2). Under 1 atm of H_2 , hydrogenation of hex-1-ene to *n*-hexane was observed together with the formation of hex-2-enes, which were more slowly reduced to hexane. Further data on this isomeriza-



Scheme 1. Hydrogenation of 4-*t*-butylmethylenecyclohexane with osmium complex **1** [6].



Scheme 2. Hydrogenation of hex-1-ene and cyclohexene with osmium complex **6** [8].

tion/reduction reaction were later reported by the same research group [10]. Under the same reaction conditions, but at 100 °C, hex-1-ene (**7**) was rapidly isomerized to a mixture of *trans*- (**8**) and *cis*-hex-2-ene (**9**) (after 5 h, **7**:**8**:**9** = 11:65:24); no double-bond migration to the 3-position occurred, even after reaction for 24 h. Under H_2 at atmospheric pressure, hex-1-ene and *trans*-hex-2-ene were both isomerized to the same equilibrium mixture. Hydrogenation to *n*-hexane (**10**) occurred simultaneously, albeit at a much slower rate (after 5 h, **7**:**8**:**9**:**10** = 7:51:18:24); at longer reaction times, *n*-hexane became the major product (after 16 h, **7**:**8**:**9**:**10** = 3:34:7:56). Complex **6** did not hydrogenate cyclohexene under 1 atm of H_2 , but rapid conversion to cyclohexane was achieved by increasing the H_2 pressure to 5 atm (Scheme 2) [8]. The selective hydrogenation in toluene of the α,β -unsaturated aldehyde crotonaldehyde afforded the saturated alcohol or the fully reduced product, depending on the reaction conditions (Table 1, entries 1 and 2) [8]. The same reduction in 2-ethoxyethanol solution was next studied using complex **6** and other osmium and ruthenium complexes (Table 1, entries 3–9) [11]. The results show that the ruthenium complexes gave high selectivities for C=C bond reduction, whereas osmium complexes gave selective reduction of the C=O bond.

The complex $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$ was the first example of an active osmium-based catalytic system for the selective hydrogenation of conjugated and unconjugated dienes [10]. 1-Cyclohexa-1,3-diene (**11**) was isomerized under N_2 to the deconjugated product cyclohexa-1,4-diene (**12**) (after 5 h, **11**:**12** = 72:28), but at a slower rate than that observed for hex-1-ene. Under 1 atm of H_2 , hydrogenation of **11** gave the mono-olefin cyclohexene **13**, the isomerized diene **12**, and a small quantity of the fully hydrogenated product cyclohexane (**14**) (after 24 h, **11**:**12**:**13**:**14** = 37:18:42:3). Alkene **13** was slowly hydrogenated to alkane **14** under these reaction conditions (after 40 h, **13**:**14** = 83:17), but rapid reduction to **14** was achieved by raising the H_2 pressure to 5 atm. The activity of complex **6** was further investigated based on the hydrogenation of l-carvone (**15**), a model compound containing exocyclic and endocyclic C=C bonds and a carbonyl group. As shown in Scheme 3, the exocyclic C=C bond in **15** was specifically reduced under 1 atm of H_2 at 100 °C (30 turnovers in 24 h). Raising the H_2 pressure to 5 atm resulted in reduction of both C=C bonds (65 turnovers in 5 h), but the fully hydrogenated product, 2-methyl-5-(1-methylethyl)cyclohexanol, was not detected.

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