The first example of the catalytic activity of (-H)Os_3(-OCNR^{1}R^2)$(CO)_{10}$ clusters in the double bond migration reactions of allylic systems functionalised with an amido group

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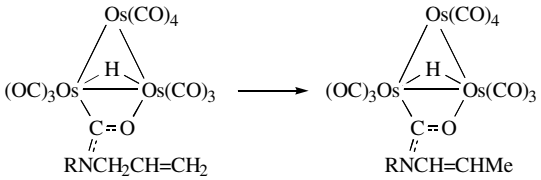
As exemplified by the isomerisation of *N*-allylacetamide in the presence of hydridocarbonyl complexes (-H)Os_3(-OCNR^{1}R^2)$(CO)_{10}$ (R^1 = H, Alk; R^2 = Alk), it has been demonstrated for the first time that they are effective catalysts for the [1,2]-double bond shift under mild conditions in allylic compounds functionalised with an amido group.

Allylic isomerisation of various olefinic molecules is the key step in many preparations. The choice of a means and conditions to start this process depends on the type of functional substituent present in the allylic fragment. In particular, even such strong bases as potassium *tert*-butoxide are known to be ineffective in the transformation of *N*-allylamides into enamides important for organic synthesis, but the [1,2]-double bond shift can be carried out in rather severe conditions in the presence of metallocomplex catalysts. The modest list of these complexes includes, to our knowledge, only the complexes of iron, $Fe(CO)_5$ under UV irradiation,[1] ruthenium, $HRuCl(PPh_3)_3$[2] and rhodium, $HRh(PPh_3)_4$,[2] Rh^I–BINAP† [3] and polymer-supported Rh^I-DIOP‡ [2,4] under heating. As regards the cluster complexes, any data on the isomerisation of alkenes with an amido function are still lacking in the literature while a sufficiently large number of papers is devoted to other types of allylic substrates (mainly to hydrocarbons and alcohols) (see review 5 and corresponding references). The pioneering work of a A. J. Deeming and S. Hasso[6] was the first example of a metal cluster-catalysed isomerisation of an unfunctionalised olefin. The high activity under mild conditions of unsaturated complex (-H)$_2Os_3(CO)_{10}$ was demonstrated. At the same time it was shown that another triosmium hydride (-H)-Os_3(-Br)$(CO)_{10}$ does not catalyse alkene isomerisation at room temperature (-Br is a 3e-donor).

In the present paper we consider the ability of the coordinatively saturated triosmium complexes (-H)Os_3(-OCNR^{1}R^2)$(CO)_{10}$, (R^1 = H, Alk; R^2 = Alk) to catalyse the isomerisation of *N*-allylamides under rather mild conditions.

We have recently described[7,8] the isomerisation of the hydridocarbonyl allyl-containing clusters (-H)Os_3(-OCNRCH$_2$CH=CH$_2$)-$(CO)_{10}$ (**1** R = H, **2** R = Me) to the propenyl-carboxamido clusters (-H)Os_3(-OCNRCH=CHMe)$(CO)_{10}$ (**3** R = H, **4** R = Me) under mild conditions (Scheme 1).



1 R = H
2 R = Me

3 R = H
4 R = Me

Scheme 1

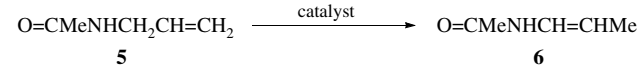
This reaction seemed to occur for no apparent reason and was obscure. Here we show that this process is a catalytic interaction.

Each of the compounds **1** and **2** can be considered as a derivative of *N*-allylamide with the corresponding cluster-containing substituent. To clarify the role of this cluster-containing substituent in the allylic isomerisation comparative tests of *N*-allylacetamide **5** and cluster **1** were performed under the same conditions. The reaction was monitored by ^{1}H NMR spectroscopy. It was found that the *N*-allylacetamide, consumed in a ~30-fold molar excess with respect to **1**, is completely converted in its presence into *N*-propenylacetamide **6**§ which is a ~1:3.5 mixture of *cis*- and *trans*-isomers ($CDCl_3$, 18 °C, ~500 h).

Cluster **1** itself is also almost fully isomerised to **3**.¶ A similar transformation of **5** (full or partial) is observed in solutions containing 3–10 mol% of the other carboxamido complexes (-H)Os_3(-OCNR^{1}R^2)$(CO)_{10}$, including those without either double bond or NH hydrogen atom (Scheme 2,†† Figure 1). No detectable spectral changes for the complexes in either form or intensity of resonances were observed during the reaction. Compound **5** appeared to be unaffected by other types of complexes such as amido (-H)Os_3(-NHCH$_2$CH=CH$_2$)$(CO)_{10}$‡‡ **10** or pure carbonyl $Os_3(CO)_{12}$ under the same conditions.

The above data demonstrate that the cluster fragment plays no significant role as the substituent in the convertible allyl-containing molecule (double bond migration occurs in compound **5** lacking this substituent but only in the presence of any carboxamido cluster), and the allylic isomerisation in itself is not a monomolecular process. We are obviously dealing with a catalytic type of reaction, in which the cluster fragment (-H)Os_3(-OCN) takes part.

To confirm these findings, comparative estimates (^{1}H NMR) for **2** to **4** conversion rates have been obtained, depending on



5 **6**

catalyst = (-H)Os_3(-OCNR^{1}R^2)$(CO)_{10}$

1 R^1 = H, R^2 = Allyl
2 R^1 = Me, R^2 = Allyl
7 R^1 = H, R^2 = Me
8 R^1 = H, R^2 = $(CH_2)_4$Me
9 R^1 = R^2 = Me

Scheme 2

† BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.

‡ DIOP = 2,3-isopropyliden-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane.

§ *trans*-**6**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.67 (br. s, 1H, =NH), 6.72 (ddq, 1H, =N–C H=, ^3J 14.2, 10.3 Hz, ^4J 1.7 Hz), 5.12 (dq, 1H, =CH–, ^3J 14.2 Hz, ^3J 6.8 Hz), 2.02 [s, 3H, –C(O)Me], 1.66 (dd, 3H, Me, ^3J 6.8 Hz, ^4J 1.7 Hz).

cis-**6**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.29 (br. s, 1H, =NH), 6.70 (ddq, 1H, =N–C H=, ^3J 9.0, 10.7 Hz, ^4J 1.8 Hz), 4.80 (dq, 1H, =CH–, ^3J 9.0 Hz, ^3J 7.1 Hz), 2.09 [s, 3H, –C(O)Me], 1.63 (dd, 3H, Me, ^3J 7.1 Hz, ^4J 1.8 Hz).

¶ Like **1**, complex **3** may also exhibit catalytic activity. However, a decrease in the reaction rate with time indicates that the activity of **3** cannot be higher than that of **1**.

†† Syntheses of **7**, **9**: see ref. 9 and of **8**, see ref. 10.

‡‡ *Synthesis of* **10**: sealed tube, a mixture of (-H)Os_3(-OH)$(CO)_{10}$ and $NH_2CH_2CH=CH_2$ (1:2) in THF, 90 °C, 1 h. Yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.85 (ddt, 1H, =CH–, $^3J_{trans}$ 16.1 Hz, $^3J_{cis}$ 10.3 Hz, ^3J 6.5 Hz), 5.30 (dd, 1H, =CHH_{cis}, ^3J 10.3 Hz, J_{gem} 1.1 Hz), 5.24 (dd, 1H, =CHH_{trans}, ^3J 16.1 Hz, J_{gem} 1.1 Hz), 3.95 (br. s, 1H, =NH), 3.46 (dd, 2H, =NCH$_2$–, ^3J 6.5 Hz, $^3J_{CH–NH}$ 6.9 Hz), –4.90 (d, 1H, -H, ^3J 2.7 Hz). IR data are analogous to those described in the literature.[11]

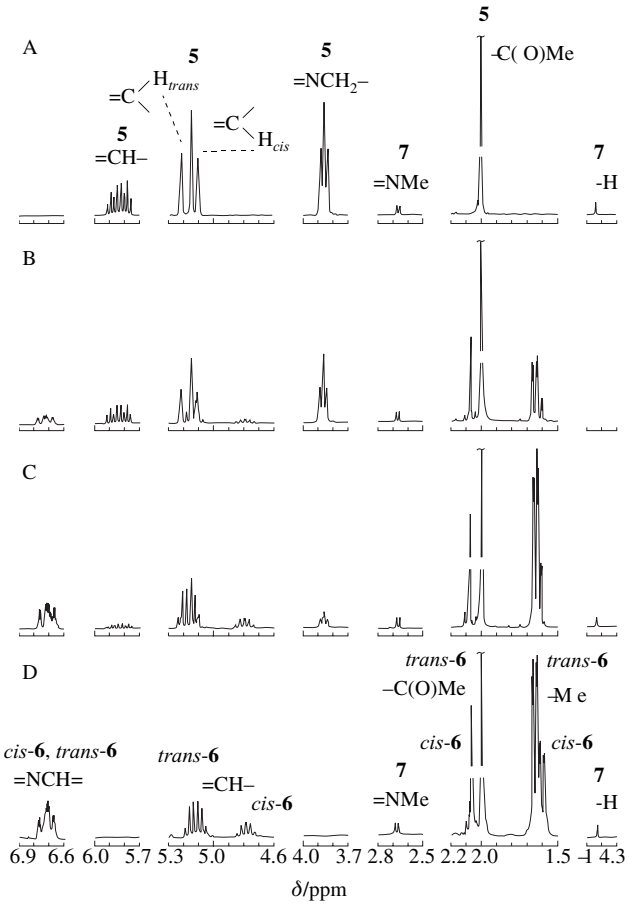


Figure 1 Changes in the ^{1}H NMR spectra over 1 week for the main resonances from *N*-allylacetamide **5** mixed with 3 mol% of (-H)Os_3(-OCNHMe)$(CO)_{10}$ **7** in $CDCl_3$ solution (250 MHz, room temperature). The mole fraction of *N*-propenylacetamide **6** increases gradually from zero (A) through 30% (B) and 85% (C) to 100% (D).

both the concentration of **2** and the presence in its solution of any other Os_3 cluster having a carboxamido bridging ligand. It was found that the reaction rate, as expected, increases as the general cluster concentration grows and depends on the kind of -ligand present. Specifically, for a solution of **2** in $CDCl_3$ 0.015 mol dm^{-3} (*a*) at 20 °C the reaction halftime $t_{1/2} \approx 536$ h, while for 0.045 mol dm^{-3} (*b*) the estimated $t_{1/2}$ value is ~317 h, which is approximately 1.7 times less. After the addition of complex **7** to the solution (*a*) and reaching the same overall concentration as for (*b*) (*i.e.* 0.03 mol dm^{-3} for **7**), $t_{1/2}$ (~177 h) decreases [1.8 times with respect to (*b*) and 3 times with respect to (*a*)]. Similarly, the halflife decreases by approximately 3.2 times (from ~863 h to ~266 h) when passing from solution **2** (0.023 mol dm^{-3} in C_6D_6) to a mixture of **2** with complex **9** (0.047 mol dm^{-3}).

Hence the examples of isomerisation of (-H)Os_3(-OCN-$RCH_2CH{=}CH_2$)$(CO)_{10}$ clusters (R = H, Me) and *N*-allylacetamide in the presence of hydridocarbonyl complexes (-H)-Os_3(-OCNR^1R^2)$(CO)_{10}$ (R^1 = H, Alk; R^2 = Alk) demonstrate that a [1,2]-double bond shift, at least of a monosubstituted bond, in the allylic systems functionalised with an amido group is invoked by these complexes, even at room temperature.

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