

ACTIVATION OF C-H BONDS IN SATURATED HYDROCARBONS. THE CATALYTIC FUNCTIONALISATION OF CYCLOOCTANE BY MEANS OF SOME SOLUBLE IRIDIUM AND RUTHENIUM POLYHYDRIDE SYSTEMS

Hugh Felkin, Tauqir Fillebeen-Khan,<sup>\*\*</sup> Yvonne Gault,<sup>\*\*</sup>  
Rupert Holmes-Smith, and Janusz Zakrzewski

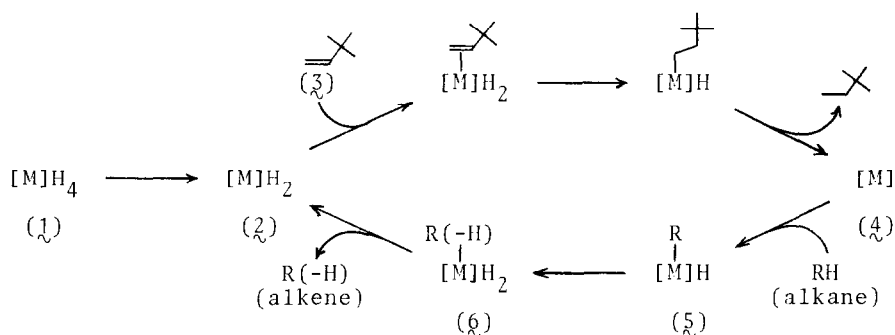
Institut de Chimie des Substances Naturelles, C.N.R.S.,  
91190 Gif-sur-Yvette, France.

Summary.- Homogeneous catalytic dehydrogenation of cyclooctane into cyclooctene has been effected by means of a variety of iridium and ruthenium polyhydrides, at 150°C, in the presence of an olefin as the hydrogen acceptor; best results (45-70 catalytic turnovers) have been achieved with  $(iPr_3P)_2IrH_5$ ,  $[(p-F-C_6H_4)_3P]_2IrH_5$  and  $[(p-F-C_6H_4)_3P]_3RuH_4$ .

Heterogeneous reactions (reforming, hydrocracking) involving alkanes, used on a large scale industrially, require vigorous conditions and are very unselective.<sup>1</sup> Homogeneous transition metal catalysts are often milder and more selective than their heterogeneous counterparts,<sup>2</sup> and current interest<sup>3</sup> in the "activation" of saturated hydrocarbons by soluble transition metal compounds is sustained by the prospect of finding a system which would allow the efficient, selective, catalytic, functionalisation of these rather unreactive substrates. Although a few soluble systems (containing Pt,<sup>4</sup> Ir,<sup>5</sup> Re,<sup>6</sup> Rh,<sup>7</sup> Lu and Y<sup>8</sup>) have recently been discovered which bring about the insertion of the transition metal into the C-H bonds of saturated hydrocarbons, in only one case has such a reaction actually led to catalysis: cycloalkenes are formed catalytically from cycloalkanes when these are treated with the bisphosphine rhenium heptahydrides  $(Ar_3P)_2ReH_7$  ( $1a$ ) and an olefin (e.g.,  $3$ ) as a hydrogen acceptor.<sup>6b,9</sup>

We imagine that this homogeneous catalytic dehydrogenation proceeds by the mechanism shown in the Scheme,<sup>10</sup> via highly reactive 14e intermediates such as  $4a$  (which may exist in equilibrium with cyclometalated intermediates), and that the maximum number of catalytic turnovers which can be achieved [about 10 in the reaction involving cyclooctane and  $1a$  (Ar = p-F-C<sub>6</sub>H<sub>4</sub>)] is limited by competition between the C-H insertion step ( $4a \rightarrow 5a$ ) and various deactivation processes [e.g., oligomerisation or further dehydrogenation (by  $3$ ) of the 14e intermediates  $4a$ ].

We were interested to find out whether other soluble 18e transition metal polyhydride systems, which should be capable of affording reactive 14e intermediates  $\lambda$  in the same way (see Scheme), would also convert alkanes into alkenes. We hoped we might find a system which would deactivate less readily and thus lead to a greater number of catalytic turnovers.



Scheme. Postulated catalytic cycle for the dehydrogenation of saturated hydrocarbons by soluble 18e transition metal polyhydrides  $\lambda$ .

$[M] = \lambda, (Ar_3P)_2ReH_5$ ;  $\mu, (iPr_3P)_2IrH_5$ ;  $\nu, [(p-F-C_6H_4)_3P]_2IrH_5$ ;  
 $\rho, (Me_3P)_2IrH_5$ ;  $\sigma, [(p-F-C_6H_4)_3P]_3RuH_4$ ;  $\tau, (Ph_3P)_3RuH_4$ .

We have therefore examined the reactions of a variety of ruthenium and iridium polyhydrides with cyclooctane,<sup>11</sup> and found that the iridium pentahydrides  $(iPr_3P)_2IrH_5$  ( $\mu$ )<sup>12</sup> and  $[(p-F-C_6H_4)_3P]_2IrH_5$  ( $\nu$ )<sup>13</sup> and the ruthenium tetrahydride  $[(p-F-C_6H_4)_3P]_3RuH_4$  ( $\sigma$ )<sup>14</sup> are indeed more effective catalysts than the rhenium heptahydride  $\lambda$  ( $Ar = p-F-C_6H_4$ ) for the dehydrogenation of this cycloalkane. Deoxygenated solutions of the polyhydrides  $\mu$ ,  $\nu$  and  $\sigma$  (2 mM) and 3,3-dimethylbutene ( $\lambda$ ) (200 mM) in cyclooctane were heated at 150°C in evacuated sealed tubes<sup>15</sup> until no further reaction occurred. The iridium pentahydride  $\mu$  gave 23 catalytic turnovers after 3 hours and reached a maximum of 70 turnovers (*i.e.*, 70 moles of cyclooctene<sup>16</sup> were formed per mole of  $\mu$ ) after 5 days; the ruthenium tetrahydride  $\sigma$  gave 45-55 turnovers after 10 days; and the iridium pentahydride  $\nu$  gave 30-35 turnovers after 5 days. When the initial quantity of olefin  $\lambda$  was halved ( $\nu$  2 mM, and  $\lambda$  100 mM), after 8 days it was almost entirely converted to 2,2-dimethylbutane (g.c.) and 45 moles of cyclooctene per mole of  $\nu$  were formed (corresponding to a yield of 90% with respect to  $\lambda$ ). Presumably  $\lambda$  and cyclooctane compete for the reactive intermediate capable of inserting into a C-H bond of cyclooctane.

The polyhydrides  $(Me_3P)_2IrH_5$  ( $\rho$ )<sup>17</sup> and  $(Ph_3P)_3RuH_4$  ( $\tau$ )<sup>18</sup> also catalysed the formation of cyclooctene<sup>19</sup> from cyclooctane under the same conditions but they were less effective than  $\mu$ ,  $\nu$  and  $\sigma$ .

The solutions were colourless ( $\mu$ ), yellow ( $\nu$ ,  $\sigma$ ), or orange ( $\rho$ ,  $\tau$ ) at the start of the reactions, and brown at the end. They appeared to be perfectly homogeneous throughout, and the presence of mercury did not significantly

affect the yields of cyclooctene, indicating that colloidal metal was not involved.<sup>20</sup> Furthermore, samples of the ruthenium tetrahydride  $1e$ , recrystallised from different solvent systems,<sup>21</sup> were equally effective as catalysts, suggesting that the catalytically active species is derived from the tetrahydride rather than from a trace impurity.

This approach to the catalytic dehydrogenation of cycloalkanes thus appears to be quite general. We believe that systems such as  $1$ , which are capable of forming  $14e$  intermediates (see Scheme), are more likely to lead to efficient catalysis than systems involving only  $16e$  intermediates. Not only are  $14e$  complexes expected to be more reactive than related  $16e$  complexes in the key C-H insertion step (e.g.,  $4 \rightarrow 5$ ), but catalysis requires the regeneration of a reactive intermediate, and this can be achieved when the product of the C-H insertion step is itself still coordinatively unsaturated ( $16e$ ) and therefore able to undergo further reaction (e.g.,  $\beta$ -elimination, followed by loss of olefin,  $5 \rightarrow 6 \rightarrow 2$ ).<sup>22</sup>

#### References and Footnotes

1. H. Pines, "The Chemistry of Catalytic Hydrocarbon Conversions", Academic Press, New York, 1981.
2. G.W. Parshall, "Homogeneous Catalysis", John Wiley and Sons, New York, 1980; C. Masters, "Homogeneous Transition-Metal Catalysis", Chapman and Hall, London, 1981.
3. R. Dagani, Chem.Eng.News, Jan.18, 1982, p. 59; J. Haggin, ibid., Feb. 14, 1983, p. 9; T.H. Maugh, Science, 1983, 220, 1261.
4. A.E. Shilov, Soviet Sci.Revs Sect.B.,Chem.Revs, 1982, 4, 71; G.B. Shul'pin, G.V. Nizova and A.E. Shilov, J.Chem.Soc.,Chem.Commun., 1983, 671.
5. R.H. Crabtree, J.M. Mihelcic, and J.M. Quirk, J.Am.Chem.Soc., 1979, 101, 7738; R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, and J.M. Quirk, ibid., 1982, 104, 107; A.H. Janowicz and R.G. Bergman, ibid., 1982, 104, 352 and 1983, 105, 3929; J.K. Hoyano and W.A.G. Graham, ibid. 1982, 104, 3723; J.K. Hoyano, A.D. McMaster, and W.A.G. Graham, ibid., 1983, 105, 7190.
6. (a) D. Baudry, M. Ephritikhine, and H. Felkin, J.Chem.Soc.,Chem.Commun., 1980, 1243 and 1982, 606; D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, ibid., 1982, 1235; M.A. Green, J.C. Huffman, K.G. Caulton, W.R. Rybak, and J.J. Ziolkowski, J.Organometal.Chem., 1981, 218, C39; (b) D. Baudry, M. Ephritikhine, H. Felkin, and R. Holmes-Smith, J.Chem.Soc.,Chem.Commun., 1983, 788; (c) accompanying paper: D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, Tetrahedron Letters, 1984, 25,
7. W.D. Jones and F.J. Feher, Organometallics, 1983, 2, 562.
8. P.L. Watson, J.Am.Chem.Soc., 1983, 105, 6491.
9. The presence of a hydrogen acceptor is necessary, for thermodynamic reasons, in catalytic dehydrogenations, since the reaction: alkane  $\rightarrow$  alkene +  $H_2$  is endergonic.

10. All the individual steps in the Scheme must be reversible; the system is driven clockwise (as shown) by the large concentration gradient between the alkane RH (ca. 10M) and 2,2-dimethylbutane (< 0.1M).
11. We have mainly used cyclooctane as the substrate since it has a convenient boiling point (150°C), and it gave the best results with the rhenium systems;<sup>6b</sup> it contained no detectable cyclooctene (< 2 ppm by g.c.).
12. M.G. Clerici, S. Di Gioacchino, F. Maspero, E. Perrotti, and A. Zanobi, J.Organometal.Chem., 1975, 84, 379.
13.  $\text{Ir}(\text{C})$  (prepared by the method described for " $(\text{Ph}_3\text{P})_2\text{IrH}_3$ " by L. Malatesta, G. Caglio, and M. Angoletta, J.Chem.Soc., 1965, 6974, except that  $\text{LiAlH}_4$  in THF was used in the reduction step instead of  $\text{NaBH}_4$  in MeOH):  $^1\text{H}$  nmr ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (from TMS) 7.4 and 7.0 (m, Ar-H) and -9.05 (t,  $\underline{J}$  = 13 Hz, Ir-H);  $^{31}\text{P}$ {Ar-H} nmr ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (downfield from external  $\text{H}_3\text{PO}_4$ ) 10.04 (sextet,  $\underline{J}$  = 13 Hz).
14.  $\text{Ru}(\text{C})$  (prepared in the same way as  $\text{Ir}(\text{C})$ <sup>18</sup>):  $^1\text{H}$  nmr ( $\text{C}_6\text{D}_6$ ),  $\delta$  (from TMS) 7.3 and 6.6 (m, Ar-H) and -7.5 (m, Ru-H).
15. Preliminary experiments carried out in Schlenk tubes at or near the reflux temperature under an atmosphere of argon gave erratic results, presumably because of the volatility of the olefin  $\text{C}_8$ .
16. The yields of cyclooctene were determined by g.c. (silicone SE30 column). The olefin was isolated as its  $\text{AgSbF}_6$  salt and identified by its mass spectrum except in the reaction involving  $\text{Ru}(\text{C})$  in which cyclooctene was identified by g.c.-m.s.
17. E.K. Barefield, Inorg.Synth., 1974, 15, 34.
18. R.O. Harris, N.K. Hota, L. Sadavoy, and J.M.C. Yuen, J.Organometal.Chem., 1973, 54, 259.
19. In these reactions, cyclooctene was identified by its g.c. retention time only.
20. P. Foley, R. DiCosimo, and G.M. Whitesides, J.Am.Chem.Soc., 1980, 102, 6713; D.R. Anton and R.H. Crabtree, Organometallics, 1983, 2, 855.
21. The ruthenium tetrahydride  $\text{Ru}(\text{C})$  was recrystallised from either benzene and MeOH or ether and hexane. From the latter solvent system  $\text{Ru}(\text{C})$  crystallised as  $[(\text{p-F-C}_6\text{H}_4)_3\text{P}]_3\text{RuH}_4 \cdot 3/4 \text{C}_4\text{H}_{10}\text{O}$  (confirmed by  $^1\text{H}$  nmr).
22. We thank Dr. B.C. Das (Gif) for the mass spectra, Mr. J.M. Dedieu (Orsay) for the g.c.-m.s. analysis, Roussel-Uclaf S.A. (Paris) for a fellowship (to R.H.S.), and the Compagnie des Métaux Précieux (Ivry) for a generous loan of iridium and ruthenium.

(Received in France 15 January 1984)