# Selective Isomerization of Methylpentanes on Iridium Catalysts

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*Summary* The very fast isomerization of 2-methyl[2-$^{13}$C]pentane to 3-methyl[3-$^{13}$C]pentane and the selective hydrogenolysis of methylcyclopentane to methylpentanes on iridium suggest the participation of metallocarbenes and metallocarbynes as reaction intermediates.

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IRIDIUM is a very active catalyst for the hydrogenolysis of alkanes[1] and the isomerization of neopentane to isopentane.[2] However, isomerization of n-butane, n-pentane, and n-hexane was not observed under similar conditions.[3] We therefore decided to investigate in detail the isomerization of hexanes on 10% Ir–Al$_2$O$_3$ and on iridium sponge catalysts.

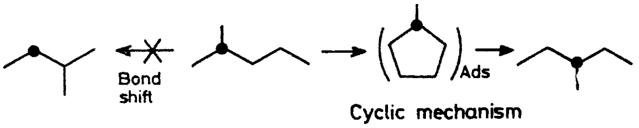
Isomerization of 2-methylpentane to 3-methylpentane and the reverse reaction occur with rates comparable to that of hydrogenolysis, while interconversion between methylpentanes and n-hexane is almost undetectable (Table 1).

TABLE 1. Initial product distributions.

| | | Reaction products (weight %) | | | | | Reactivity factors:[b] cleavage of | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reactant | Catalyst[a] | 2-Methyl pentane | 3-Methyl-pentane | n-Hexane | Methylcyclo-pentane | Sh[c] | $C_t$–$C_p$ | $C_t$–$C_s$ | $C_s$–$C_s$ | $C_s$–$C_p$ |
| 2-Methylpentane | A | — | 28·1 | 2·0 | 0·5 | 67 | 0·4 | 0·5 | 2·5 | 1·2 |
| ,, | B | — | 43·5 | 0·0 | 2·5 | 48 | 0·35 | 0·3 | 2·25 | 1·75 |
| 3-Methylpentane | A | 44·1 | — | 0·3 | 1·2 | 50 | 0·15 | 0·6 | — | 1·8 |
| ,, | B | 49·7 | — | 0·0 | 0·1 | 40 | 0·1 | 0·2 | — | 2·25 |
| n-Hexane | A | 0·2 | 0·2 | — | 0·0 | 98·3 | — | — | 1·1[d] | 0·5 |
| ,, | B | 0·4 | 0·3 | — | 0·0 | 89·3 | — | — | 1·85[e]<br>0·85[d] | 1·0 |
| Methylcyclopentane | A | 73·4 | 26·0 | 0·3 | — | 99·7 | | | 1·25[e] | |
| ,, | B | 69·7 | 28·7 | 0·4 | — | 98·2 | | | | |

[a] A: Ir–Al$_2$O$_3$ at 433 K; B: Ir sponge at 443 K. [b] Observed rate divided by statistical rate of hydrogenolysis (G. Leclercq, L. Leclercq and R. Maurel, *J. Catalysis*, 1977, **50**, 87). [c] Percentage of the products obtained by a one-bond rupture mechanism. [d] C(2)–C(3) and C(4)–C(5) bonds. [e] C(3)–C(4) bond.

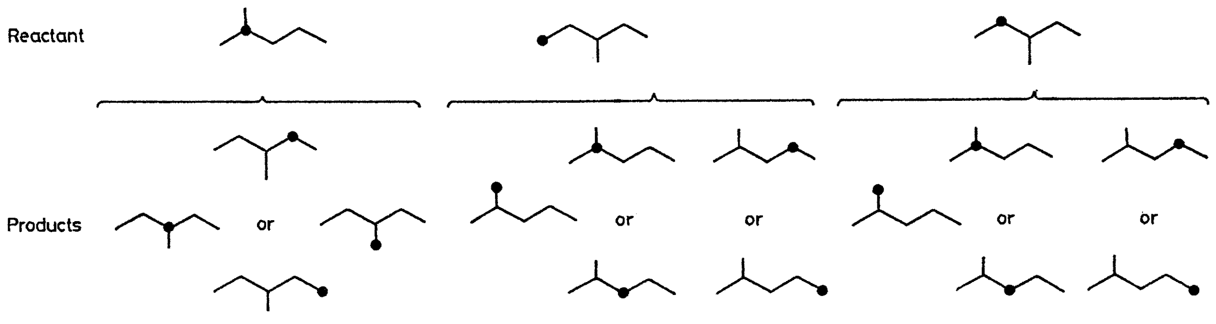
Isomerizations of 2-methyl[2-$^{13}$C]pentane, 3-methyl[1-$^{13}$C]pentane, and 3-methyl[2-$^{13}$C]pentane were therefore investigated to distinguish between the two reaction mechanisms commonly believed to be involved in skeletal rearrangements on metal:[4] carbocyclic and bond shift. Within the experimental error (±2% for each species[5]), the results (Table 2) are consistent with a carbocyclic mechanism (Scheme 1).



SCHEME 1. ● = $^{13}$C.

The hydrogenolysis of methylcyclopentane, which yields 2-methylpentane and 3-methylpentane, but not n-hexane (Table 1), the fast interconversion of 3-methylhexane and ethylpentane, and the failure of 2-methylhexane and n-heptane to isomerize confirm that the major isomerization mechanism on iridium is a selective carbocyclic mechanism in which only secondary–secondary CH$_2$–CH$_2$ cyclic bonds are formed and ruptured. Since the dehydrocyclisation step requires the presence in the molecule of two primary carbon atoms in 1 and 5 positions, it is possible that the

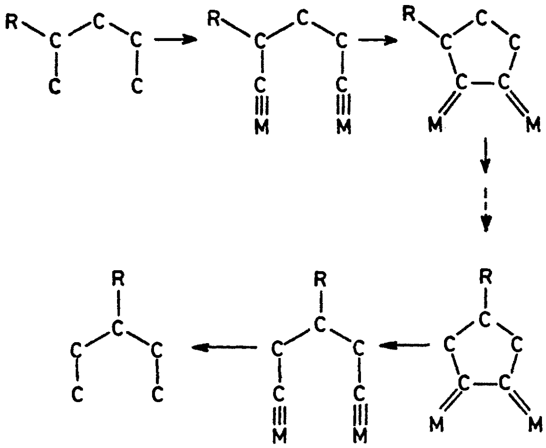
TABLE 2. Isomerization: distribution (%) of the isotopic varieties.[a]



| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Bond shift | 0 | 100 | 0 | 50 | 0 | 50 | 0 | 50 | 50 |
| Cyclic mechanisms | 100 | 0 | 0 | 0 | 0 | 100 | 50 | 50 | 0 |
| Observed | 100 | 0 | 0 | 2 | 0 | 98 | 51·5 | 46·5 | 2 |

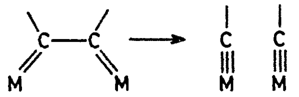
[a] ● = $^{13}$C.

reaction proceeds *via* a dicarbyne intermediate attached to two metal atoms (Scheme 2).



SCHEME 2. R = Me or Et.

Metallocarbenes have been proposed as possible intermediates in exchange of hydrocarbons with deuterium.[6] Also, the importance of metallocarbenes and metallocarbynes in selective and extensive hydrogenolysis of hydrocarbons on cobalt has been emphasized.[7] On iridium, where hydrogenolysis occurs mainly *via* cleavage of one carbon–carbon bond, secondary–secondary ($C_s$–$C_s$) and secondary–primary ($C_s$–$C_p$) bonds are ruptured much more rapidly than tertiary–primary ($C_t$–$C_p$) and tertiary–secondary ($C_t$–$C_s$) bonds (Table 1). This suggests that hydrogenolysis of alkanes, like that of alkylcyclopentanes, involves formation of two double bonds between the metal and two contiguous carbon atoms (Scheme 3).



SCHEME 3

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