

Preliminary communication

Hyrido complexes of zirconium

IV. Reactions with olefins

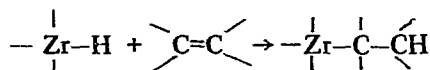
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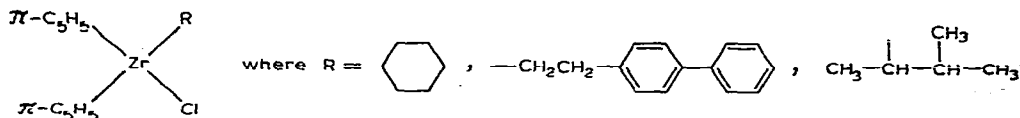
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Part III of this series¹ described the addition of the zirconium hydrides $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(H)Cl}$ to acetylenes to give alkenylzirconium derivatives. We now report the reactions of these hydrides with olefins to give saturated compounds.

The difficulty in preparing alkyl derivatives of transition metals is connected with their thermal instability and general lability which renders their isolation difficult. Thermal instability of alkyls is in many cases due to ease of β -elimination of hydrogen²⁻⁴ which explains why methyl derivatives of zirconium, e.g. $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(CH}_3)_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(CH}_3\text{)Cl}$, are relatively stable^{5,6} while the corresponding ethyl derivatives are considerably less so (in fact only $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(C}_2\text{H}_5\text{)Cl}$ has been isolated⁷). It was to be expected, therefore, that under the conditions used for the preparation of alkenylzirconium derivatives, namely addition of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(H)Cl}$ to acetylenes in boiling benzene¹, alkyl derivatives formed from these hydrides and olefins would not be isolable, since the method of preparation ensures the presence of a β -hydrogen atom.

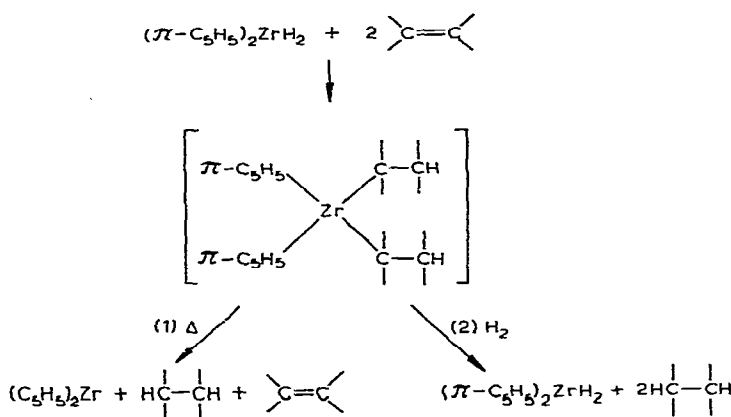


Such has proved to be the case but by using lower temperatures and longer reaction times (typically, room temp. for several hours) it has been found possible to prepare the monoalkyl derivatives shown below from the monohydride, $(\pi\text{-C}_5\text{H}_5)_2\text{Zr(H)Cl}$ and the appropriate olefin, viz. cyclohexene, 4-vinyldiphenyl or 2-methyl-2-butene:



Satisfactory analyses have been obtained for these compounds. The point of attachment of zirconium in the second and third compounds is not known with certainty; the ^1H NMR spectra are complicated by overlapping multiplets in the aliphatic region. These alkyl derivatives are of marginal stability and decompose slowly in the solid state and more rapidly in solution.

The instability of compounds such as this can be used to advantage; *e.g.* for the synthesis of derivatives of lower-valent zirconium by pyrolysis or hydrogenolysis;



Reaction 1 occurs with the dihydride and stoichiometric amounts of olefin (2 moles); the formation of the intermediate unstable complex is shown by the dissolution of the insoluble dihydride to give a dark solution which decomposes with precipitation of a dark solid identified as zirconocene. The formation of alkane and alkene in this reaction has been demonstrated in the reaction with 4-vinyldiphenyl. Equal amounts of ethyldiphenyl and vinyldiphenyl (the latter complexed with zirconocene) were identified in the reaction product by NMR spectroscopy.

When a pressure of hydrogen was applied during the reaction of cyclohexene with the zirconium dihydride it was found that hydrogen was absorbed and the metal hydride was reformed together with cyclohexane (Reaction 2). The hydrogenation is therefore catalytic; it appears to be a general reaction for olefinic hydrocarbons (and also acetylenes) (see Table 1).

The catalyst darkens considerably during some of these hydrogenations, possibly due to the formation of zirconocene by pyrolysis of alkyl derivatives.

The monohydride $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{Cl}$, although not tested as extensively as the dihydride, will also reduce these olefins, but longer reaction times and/or higher temperatures are necessary. This lower activity is no doubt connected with the increased stability of the intermediate organozirconium derivative.

Other zirconium and titanium derivatives were found to be active hydrogenation catalysts under similar conditions, *viz.* $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)\text{Cl}$, $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)\text{Cl}$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$, $(\text{C}_5\text{H}_5)_2\text{Zr}$ and $(\text{C}_5\text{H}_5)_2\text{Ti}$. This behaviour

TABLE 1

CATALYTIC HYDROGENATION USING $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ (H_2 press. 50–100 atm)

<i>Unsaturated compound</i>	<i>Temp. (°C)</i>	<i>Product (yield is quantitative)</i>
Cyclohexene	80	Cyclohexane
<i>trans</i> -Stilbene	100	1,2-Diphenylethane
<i>cis</i> -Stilbene	100	1,2-Diphenylethane
Styrene	120	Ethylbenzene
Vinylcyclohexane	120	Ethylcyclohexane
2-Methyl-1-butene	120	2-Methylbutane
2-Methyl-2-butene	120	2-Methylbutane
<i>cis</i> -Hept-2-ene	120	Heptane
Phenylacetylene	120	Ethylbenzene
3-Hexyne	120	Hexane

was not unexpected in view of the ability of titanocene⁸ (and presumably zirconocene) to form hydrides and the facile displacement of alkyl groups from these metals under the hydrogenation conditions.

REFERENCES

- 1 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 27 (1971) 373.
- 2 H. de Vries, *Rec. Trav. Chim. Pays Bas*, 80 (1961) 866.
- 3 E. Heins, H. Hinck, W. Kaminsky, G. Oppermann, P. Raulinat and H. Sinn, *Macromol. Chem.*, 134 (1970) 1.
- 4 W. Mowat, A. Shortland, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. Dalton*, (1972) 533.
- 5 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 34 (1972) 155.
- 6 J.R. Surtees, *Chem. Commun.*, (1965) 567.
- 7 H. Sinn and G. Oppermann, *Angew. Chem. Int. Ed.*, 5 (1966) 962.
- 8 J.E. Bercaw, R.H. Marvick, L.G. Bell and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 94 (1972) 1219.

J. Organometal. Chem., 43 (1972)