Phosphinomethyl Zirconium(III) Complexes as Hydrogenation Catalysts of Specific Selectivity

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Zirconium(III) complexes containing the chelated $\overline{ZrCH_2P}Ph_2$ moiety hydrogenate unsaturated hydrocarbons in a rapid catalytic process with specific selectivity, giving a quantitative yield of cyclo-octene from 1,3- and 1,5-cyclo-octadiene and of 1,2,3,4-tetraphenylbutane from diphenylacetylene.

Whilst zirconocene hydrides such as $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ are largely used as stoicheiometric reagents for selective synthesis of various organic derivatives from alkenes and alkynes,[1] previous attempts at obtaining catalytic hydrozirconation are essentially restricted to systems using aluminium hydrides as the hydrogen source.[2]

Reports concerning the reduction of unsaturated substrates by H_2 in the presence of catalytic amounts of zirconium(IV) complexes are scarcely documented.[3] The problem in this case is to regenerate the zirconium–hydrogen bond by the action of gaseous H_2. To this end, we explored systems containing reduced zirconium complexes as precursors.

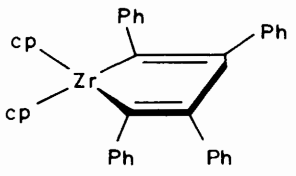
In this work, we present results on catalytic hydrogenation of olefins, diolefins, and diphenylacetylene in the presence of complexes containing the zirconium(III) chelated moiety $\overline{ZrCH_2P}Ph_2$ either generated *in situ* or separately synthesized. Unprecedented activity and quite specific selectivity characterized these systems.

We recently established that by moderate heating (60—70 °C) of a suspension of the white polymeric hydride $[(cp)_2ZrH(CH_2PPh_2)]_n$ (**1**) (cp = $\eta^5\text{-}C_5H_5$), a dark red solution of two zirconium(III) species, $(cp)_2\overline{ZrCH_2P}Ph_2$ (**2**) and '$(cp)_2ZrH$' (**3**) is readily obtained.[4] Complementary experiments performed under H_2 pressure showed that the

Table 1. Hydrogenation of olefins and diolefins.[a]

Precursor	Substrate	*n*	Reaction time/min	Conversion %	Product obtained[b]
$[(cp)_2ZrH(CH_2PPh_2)]_n$ (**1**)	hexene	300	60	100	hexane
	styrene	300	60	100	ethylbenzene
	norbornene	350	10	100	norbornane
	cyclo-octene	—	(>16 h)	—	no reaction
	penta-1,3-diene[d]	100	20	100	pentane
	penta-1,4-diene[c,d]	120	200	90	pentane
	norbornadiene	350	60	100	norbornane
	cyclo-octa-1,3-diene	350	20	100	cyclo-octene[e]
	cyclo-octa-1,5-diene[c]	350	90	100	cyclo-octene[e]
$(cp)_2\overline{ZrCH_2P}Ph_2$ (**2**)	hexene	300	20	100	hexane
	styrene	300	45	100	ethylbenzene
	penta-1,4-diene[c]	100	360	90	pentane
	cyclo-octa-1,3-diene	300	30	100	cyclo-octene[e]

[a] Experimental conditions: 80 °C; 40 bar; solvent: tetrahydrofuran; catalyst:substrate:solvent molar ratio: $1:n:\sim1000$. [b] Very high selectivity (>95%). [c] Intermediate formation of the 1,3-diene is detected. [d] Intermediate formation of pent-2-ene is detected. [e] No other product detectable.



(4)

proportion of the reduced hydride (**3**) may thus be increased, corresponding to the reaction (1). So, we decided to investigate the catalytic performances of (**1**) as a precursor for hydrogenating unsaturated substrates in a temperature range where the reduction was to take place.

$$\underset{(\mathbf{2})}{(cp)_2\overline{ZrCH_2P}Ph_2} + H_2 \rightarrow \underset{(\mathbf{3})}{\text{‘}(cp)_2ZrH\text{’}} + PPh_2Me \qquad (1)$$

From the data collected in Table 1, it appears that hydrogenation of olefins (except cyclo-octene) and conjugated diolefins is very rapid and as far as we know the system is more efficient than any homogeneous zirconium(IV) based system described till now.

The most striking result shown in Table 1 is the quantitative and completely selective formation of cyclo-octene from cyclo-octadiene (no cyclo-octane detectable). Actually, other examples of the reduction of conjugated dienes into monoenes have been previously described and discussed.[5] But to the best of our knowledge, none of these other catalytic systems is quantitatively selective (less than 100% yield, non negligible presence of cyclo-octane). In contrast complete resistance of cyclo-octene to be reduced appears as a characteristic feature of zirconium systems since cyclo-octene was found to be completely reluctant to give cyclo-octyl by stoicheiometric hydrozirconation.[6]

In order to confirm the role of Zr^{III} moieties in the catalytic process and keeping in mind reaction (1), we investigated systems where the precursor was (**2**), prepared by reduction (Na/Hg) of $(cp)_2ZrCl(CH_2PPh_2)$ as reported by Schore.[7] As can be seen in Table 1, reaction times are quite similar for both precursors and the same selectivity is observed. Moreover we performed e.s.r. measurements on the catalytic mixture during the course of the reaction. The expected formation of the hydride (**3**) is clearly visible as an increasing doublet (g = 1.987, $a\,^1H$ = 8 G†) in addition to the precursor (**2**) (g = 1.985, $a\,^{31}P$ = 19.5 G) (Figure 1).

It must be added that the hydride (**1**) is a catalyst for the isomerization of olefins and diolefins. For instance, 80 mg of (**1**) were added to 6.2 g of cyclo-octa-1,5-diene without any solvent in a sealed tube (under argon, no H_2 added) and heated to 80 °C. The conversion into cyclo-octa-1,3-diene was found to be 56% after 3.5 h, 100% after 1 day.

We also explored the catalytic hydrogenation of alkynes, especially diphenylacetylene which in the presence of zirconocene dihydrides was previously transformed into 1,2-diphenylethane.[3] In fact in the presence of (**1**) at 80 °C, 40 bar H_2 in tetrahydrofuran with catalyst : substrate = 1 : 100 molar ratio, we obtained not very rapidly (in *ca.* 20 h) the unexpected 1,2,3,4-tetraphenylbutane (as the unique product of the quantitative conversion of the substrate), identified by $T_{fus.}$ = 181 °C, ^1H n.m.r. spectroscopy, and *X*-ray structure (to be published elsewhere). This quite unprecedented result is to be related to stoicheiometric reactions of diphenylacetylene on zirconocene dihydrides which produce acetylene hydrogenation and zirconacyclopentadiene (**4**) formation as two competing processes.[8] Still more closely related to our system is the recent observation by Petersen[9] that a paramagnetic species, attributed to $(cp')_2ZrH(PhC{\equiv}CPh)$ is detected by e.s.r. spectroscopy and assumed to participate in the formation of (**4**) by a redox process involving zirconium(II), (III), and (IV) intermediate species.

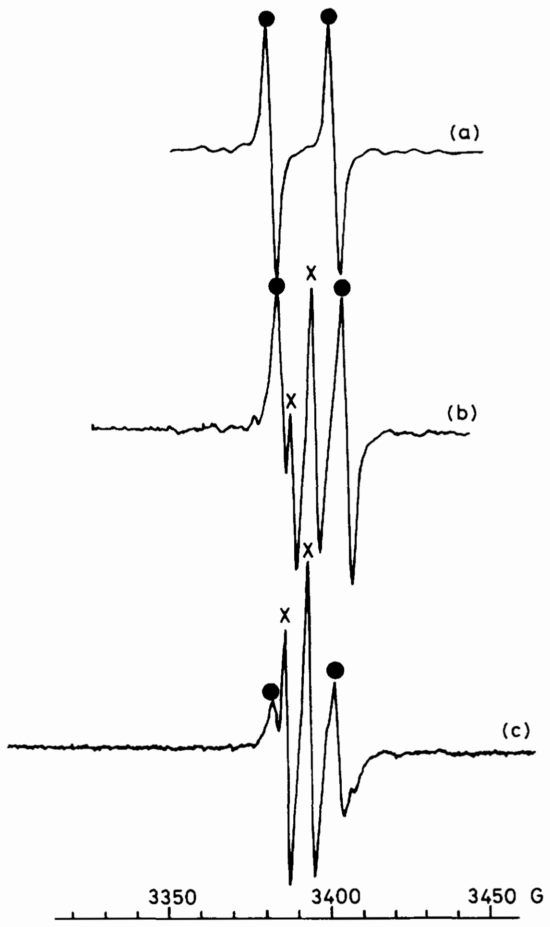


Figure 1. X-Band e.s.r. spectra registered at room temperature on samples syringed off during hydrogenation of hex-1-ene in the presence of (**2**); (a) 0% conversion; (b) about 50% conversion; (c) 100% conversion. ● attributed to (**2**); × attributed to (**3**).

The catalytic mechanism and particularly the elimination step yielding 1,2,3,4-tetraphenylbutane, as well as the dismutation of zirconium(III) invoked in the stoicheiometric formation of (**4**), are likely to involve interactions between two zirconium centres in bimolecular reactions. However, as far as we know, there is no evidence for the formation of the dizirconium cyclohexadiene complex mentioned by Wailes in a previous work.[10]

To summarize, the presence of the CH_2PPh_2 group bonded to zirconium results in strongly enhanced catalytic activity and original selective obtention of cyclo-octene from cyclo-octadiene and of 1,2,3,4-tetraphenylbutane from diphenylacetylene. Generation of the reduced hydride (**3**) is also certainly involved in the catalytic process but is influenced by the presence of the phosphino moiety since the results obtained in this work strongly differ from zirconocene dihydride systems although the latter may also generate (**3**) by

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† 1 G = 10^{-4} T.

moderate thermolysis (and photolysis).[11] It seems possible that zirconocene phosphorus ylide complexes may be involved in the mechanism, by reference to recent results concerning the rich reactivity of zirconium and hafnium ylides.[12]

Received, 6th May 1986; Com. 595

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