

Preliminary communication

SYNTHESIS AND REACTIONS OF SUBSTITUTED ZIRCONOCENE AND HAFNOCENE DIMETHYLS AND THE CORRESPONDING DIHYDRIDES

S. COUTURIER and B. GAUTHERON

Laboratoire des Organométalliques (équipe du Laboratoire de Polarographie Organique associé au CNRS, LA 33), Faculté des Sciences, 6 boulevard Gabriel 21100 Dijon (France)

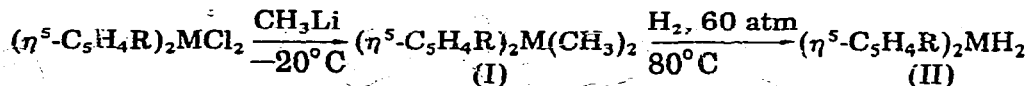
(Received July 4th, 1978)

Summary

Hydrogenolysis of $M(\text{CH}_3)_2$ ($M = \text{Zr, Hf}$) bonds gives novel substituted zirconocene and hafnocene dihydrides. The use of the optically active complex $[\eta^5\text{-C}_6\text{H}_5\text{C}^*\text{H}(\text{CH}_3)\text{C}_5\text{H}_4]$ ($\eta^5\text{-C}_5\text{H}_5$) $\text{Zr}(\text{CH}_3)_2$ as a catalyst in homogeneous hydrogenation of prochiral alkenes is reported.

Some hydrides and dihydrides of zirconocene are well known but very few of them bear cyclopentadienyl ligands [1,2] and surprisingly no hafnocene hydrides are known. We describe below the synthesis of the new dimethyl and dihydride compounds $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{ZrR}'_2$ ($\text{R}' = \text{H}$ or CH_3) and the first hafnocene compounds $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{HfR}'_2$ ($\text{R}' = \text{H}$ or CH_3). These complexes represent an approach to the synthesis of chiral dihydrides $(\eta^5\text{-C}_5\text{H}_4\text{R}^*)(\eta^5\text{-C}_5\text{H}_5)\text{MH}_2 = \text{R}^*\text{CpCpMH}_2$ ($M = \text{Zr, Hf}$) and we report the preparation of one of them in the zirconium series.

Dihydrides can often be obtained by reduction of the corresponding dichlorides by means of a metallic hydride, but the results are very dependent of the nature of the other ligands. The best general method consists of hydrogenolysis of M -carbon bonds [1] mainly of the dimethyl derivatives as follow:



($M = \text{Zr, Hf}$; $\text{R} = \text{H, Me, Me}_2\text{CH, Me}_3\text{C, PhCH}_2, \text{Ph}(\text{Me})\text{CH}$ (two stereoisomers))

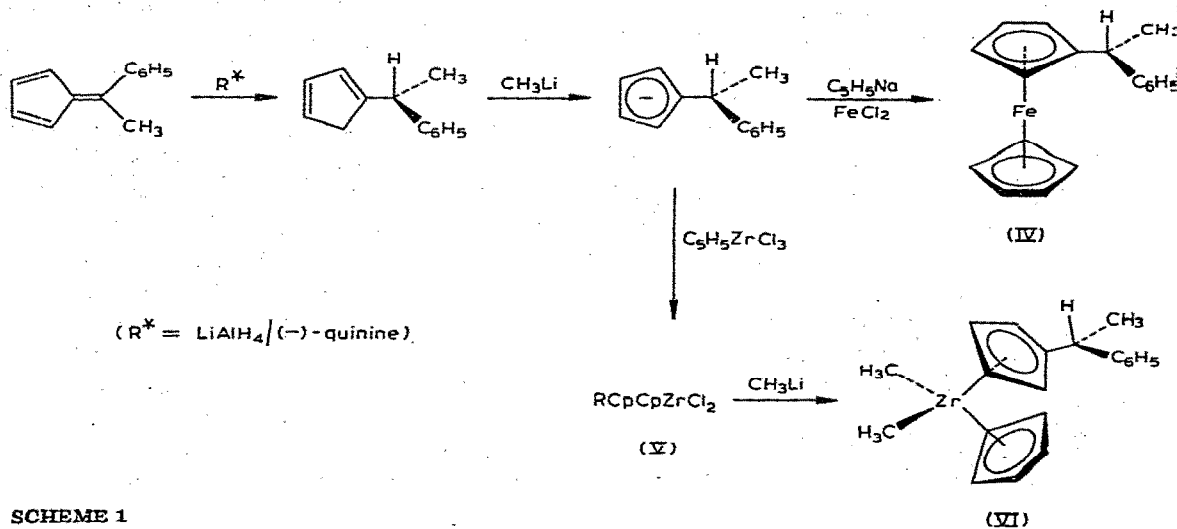
The dihydride compounds (II) are white solids, very insoluble in hydrocarbon solvents except for $\text{R} = \text{Me}_2\text{CH}$ and Me_3C (dimer products: cryoscopy). The elementary analyses and mass spectra are satisfactory. The Hf dihydrides are thermally more stable than the Zr isologs. Both are very sensitive towards air and moisture. All of them react stoichiometrically with halogens and alkyl

halides to give $(RCp)_2MX_2$ and with alcohols and phenols to give dialkoxy and diaryloxy derivatives*. We observed insertions of alkenes and alkynes, carbonyls and carbon dioxide into the $M-H$ bonds [3,4]; after hydrolysis, we obtained hydrocarbons, alcohols and methanol, respectively.

The dimethyl compounds (I) are oily or solid products very sensitive towards air, which show a $M-CH_3$ NMR signal at high field (around -0.35 ppm (Zr); -0.55 ppm (Hf); int. ref.: TMS, $CHCl_3$). They are less reactive than the dihydride complexes. In the hafnium series, they do not react with $R-X$ or $PbCl_2$ [5].

Complexes II can be used as efficient hydrogenation catalysts of alkenes and alkynes, especially when $R = Me_2CH$ and Me_3C , for which homogeneous catalysis is possible. But the dimethyl compounds I may also be used under the same conditions. Then, at 1/1000 ratio, the complexes $(\eta^5-Me_3CCp)_2MR'_2$ ($R' = CH_3$ or H) catalyse the transformation of cyclohexene, stilbene and diphenylacetylene, (20 h, $80^\circ C$, 60 atm of hydrogen pressure) into the corresponding saturated hydrocarbons. With diphenylacetylene *trans* addition occurs. At the end the catalyst is $(\eta^5-Me_3CCp)_2MH_2$, which appears in a pure state (by NMR). The limitation on the method seems to be the purity of the substrate to be hydrogenated.

We also report the synthesis and catalytic properties of the first optically active zirconocene compound $(\eta^5-C_5H_5)$ [$\eta^5-C_5H_4C^*H(CH_3)C_6H_5$] $Zr(CH_3)_2$ (III). It seemed probable to us that III could induce asymmetric induction in the hydrogenation of prochiral alkenes. III was prepared as shown in Scheme 1.



SCHEME 1

The asymmetric reduction of the starting fulvene by means of $LiAlH_4$ /(-)-quinin [6] at $-45^\circ C$ in $(C_2H_5)_2O$ gave after hydrolysis, an optically active hydrocarbon $[\alpha]_D^{25} -11.1^\circ$ ($CHCl_3$), *S* configuration. This was transformed into the corresponding anion and then allowed to react with $C_5H_5ZrCl_3$ to give the dichloride V, $[\alpha]_D^{25} + 51^\circ$ ($CHCl_3$), *R* configuration. VI was finally obtained

*We have been unable to isolate the monosubstituted complexes $(RCp)_2M(H)R'$ ($R' =$ alkyl, alkoxy, halogen) because of disproportionation in solution: $(RCp)_2M(H)R' \rightarrow (RCp)_2MH_2 + (RCp)_2MR'_2$

as a pale-yellow oil $[\alpha]_D^{22} + 20^\circ$ (C_6H_6) by reaction of CH_3Li with V.

The optical purity of the whole compounds is established by reference with the ferrocene derivative IV, the chiroptic properties of which are well known [7]. The anion used to prepare V, reacts with C_5H_5Na in the presence of $FeCl_2$ to give the ferrocenic product IV $[\alpha]_D^{22} + 35.5^\circ$ (C_6H_6), *R* configuration (lit. [6] $+ 109.5^\circ$). This result indicates 32.3% of optical purity for VI. Complex VI can be used as homogeneous catalyst in the hydrogenation of substrates bearing no polar substituents such as prochiral alkenes. We allowed VI to react in an autoclave, with α -ethylstyrene or 2-ethyl-2-hexene (molecular ratio 1/500; hydrogen pressure: 60 atm; temperature: $80^\circ C$); after 18 h of heating we obtained, respectively, $C_6H_5CH(CH_3)C_2H_5$ and $C_4H_7CH(CH_3)C_2H_5$ having no optical activity. This lack of success in the induction is probably because the distance between the reaction and chiral centers is too great.

References

- 1 H. Weigold, A.P. Bell and R.I. Willing, *J. Organometal. Chem.*, 73 (1974) C23.
- 2 J.M. Manriquez, D.R. Alister and J.E. Bercaw, *J. Amer. Chem. Soc.*, 98 (1976) 6734.
- 3 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 27 (1971) 373; 43 (1972) C32.
- 4 P. Etievant, B. Gautheron and G. Tainturier, *Bull. Soc. Chim. Fr.*, to be published.
- 5 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, 34 (1972) 155.
- 6 O. Červinka and O. Belovsky, *Coll. Czech. Chem. Commun.*, 32 (1967) 3897 and ref. therein.
- 7 J.C. Leblanc and C. Moise, *J. Organometal. Chem.*, 120 (1976) 65.