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PHOTOLYTIC CYCLOPENTADIENYL LIGAND EXCHANGE BETWEEN DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE AND RELATED SYSTEMS

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Summary

Irradition of benzene solutions of zirconocene dichloride and zirconocene-d_{10} dichloride with 313 nm light leads to the formation of zirconocene-d_5 dichloride with a quantum yield of 0.021 mol/Ei. The equilibrium constant is 2.8. Zirconocene dichloride exchanges a cyclopentadienyl ligand photolytically with bis(methylcyclopentadienyl)zirconium dichloride with the constant equal to 2.3.

Introduction

The first cyclopentadienyl photoexchange in the d^0 system, titanocene dichloride/titanocene-d_{10} dichloride, has been reported [1]. Irradiation of benzene solutions of both titanocene-d_{10} dichloride and titanocene dichloride with light of wavelengths 313, 360, 400, and 520 nm produces the exchange of the cyclopentadienyl ligand according to the following reaction (eq. 1) [2] with

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + (\eta^5\text{-}C_5D_5)_2TiCl_2 \overset{h\nu}{\rightleftharpoons} 2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5D_5)TiCl_2 \qquad (1)$$

quantum yields of 0.02, 0.005, 0.01 and 0.007 mol/Ei, respectively. The calculated equilibrium constant of eq. 1 is 4.

Exchange has also been observed in systems [3] with d^1 metal ions, dicyclopentadienylvanadium dichloride/bis(methylcyclopentadienyl)vanadium dichloride and titanocene monochloride/titanocene-d_{10} monochloride.

Since the initial studies in the photoexchange of $C_5H_5^-$ ligands have been undertaken with titanium compounds, they were extended to zirconium. We found that photoexchange also occurs in the zirconocene dichlorides.

Experimental

All preparations were carried out under dry argon or in a vacuum and all solvents were refluxed continuously with the appropriate drying agent under argon and distilled prior to use.

Materials

Di-π-cyclopentadienylzirconium dichloride was obtained from Arapahoe Chemical Company and sublimed at 150—180° C. This material was stored in the dark.

Bis(π-methylcyclopentadienyl)zirconium dichloride was prepared according to Reynolds and Wilkinson [4] with a modification. After crystallization from hot toluene, which was saturated with hydrogen chloride, the colorless material was purified by sublimation at 110—130° C.

Zirconocene-d_{10} dichloride was prepared from zirconium tetrachloride and sodium cyclopentadienide-d_5 [5] in tetrahydrofuran. The yield was about 40% based on $ZrCl_4$, m.p. 246—248° C. The deuterium content of the product obtained was evaluated by proton NMR measurement and from the intensity decrease of C—H vibrations in the IR spectrum.

Filter solutions for isolating 313 nm light were prepared as 0.0020 M K_2CrO_4 in 0.07 M K_2CO_3 (1 cm) and 0.96 M $CoSO_4$ (1.9 cm).

The benzene solutions of 10^{-3} M in each of zirconocene dichloride and zirconocene-d_{10} dichloride (or methyl derivatives) were irradiated with 313 nm light in a merry-go-round photolysis apparatus. The irradiated samples were analyzed by mass spectrometry. The valerophenone actinometer was used to determine the lamp intensity. Actinometer solutions were irradiated under essentially the same conditions as the exchange solutions. The actinometer solution was analyzed by gas chromatography. The absence of thermal exchange was demonstrated by allowing a sample solution to reflux for 72 h in the dark, and obtaining the mass spectrum of the two zirconocene dichloride species. No peak corresponding to the d_5 species appeared in the mass spectrum.

Results and discussion

When benzene solutions containing zirconocene dichloride and zirconocene-d_{10} dichloride were irradiated by 313 nm light, exchange of the cyclopentadienyl ligand between the two molecules occurred. Exchange was detected by the mass spectrum. As the photolysis time increased, the peak at *m/e* 295, corresponding to $Cp_2ZrCl_2^+$-d_5, increased when compared with the peaks at *m/e* 290 and *m/e* 300, corresponding to d_0 and d_{10} species.

A study of Table 1 indicates that zirconocene dichloride and zirconocene-d_{10} dichloride ligand exchange results in the increase of the peak at *m/e* 295 relative to those at 290 and 300.

The ratio of the intensities of the *m/e* 295 and 290 peaks, $\Gamma_{295}/\Gamma_{290}$ was computed for each irradiation time. The fractions of exchange, F, were calculated on the basis of equilibrium value of 1.86.

Ln(1 — F) vs photolysis time was plotted for each sample. The most probable slope of the line was calculated by a standard least squares treatment of

TABLE 1

MASS SPECTROGRAPHIC DATA FOR THE ZIRCONOCENE DICHLORIDE/ZIRCONOCENE-d_{10} DICHLORIDE LIGAND EXCHANGE

Time (h)	Normalized intensities (m/e)							I_{295}/I_{290}	F
	290	295	300	65	66	70	71		
0	100	8	95	100	62	84	50	0.08	0.044
1	100	13	98	100	40	88	30	0.13	0.070
2	100	24	110	100	52	90	30	0.24	0.13
4	100	15	99	100	76	86	52	0.15	0.081
8	100	21	100	100	47	86	43	0.21	0.11
16	100	31	102	100	44	86	29	0.31	0.17
24	100	40	95	100	51	86	46	0.40	0.22
36	100	74	108	100	55	84	42	0.74	0.40
48	100	96	112	100	50	84	30	0.96	0.52
60	100	136	122	100	65	87	51	1.36	0.73
71	100	186	125	100	68	85	40	1.86	1.0
83	100	185	123	100	55	85	30	1.85	1.0

the data [6], and the rate was calculated by using the McKay equation [7]. $R = 1.4 \times 10^{-8}\ M\ s^{-1}$.

The quantum yield was calculated by dividing the exchange rate by [8] the light intensity as 0.021 mol/Ei.

The equilibrium constant for the reaction 2 calculated from the intensities of

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 + (\eta^5\text{-}C_5D_5)_2ZrCl_2 \overset{h\nu}{\rightleftharpoons} 2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5D_5)ZrCl_2 \qquad (2)$$

the exchanged peaks in the mass spectrum at t_∞ was $K = (I_{295})^2/(I_{290})(I_{300}) = 2.8$.

The photolytic cyclopentadienide ligand exchange between zirconocene dichloride and bis(methylcyclopentadienyl)zirconium dichloride was observed by the increasing intensity of the peak at m/e 304, which corresponds to $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)ZrCl_2^+$:

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 + (\eta^5\text{-}CH_3C_5H_4)ZrCl_2 \overset{h\nu}{\rightleftharpoons} 2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)ZrCl_2 \qquad (3)$$

The equilibrium constant for the reaction 3 was measured as 2.3. These low figures for both exchange systems might reflect the side reaction with impurities or the simple photodecomposition at the longer photolysis times, and decomposition can be detected by UV-visible and NMR spectroscopy. The absorbance of the exchange solution at 295 nm is decreased by 20% in the 56 h photolysis for $Cp_2ZrCl_2\text{-}d_{10}$ in Cp_2ZrCl_2 system and 25% in the 24 h photolysis for $Cp_2ZrCl_2/(MeCp)_2ZrCl_2$ system. The exchange rate for eq. 3 was estimated as $1.1 \times 10^{-8}\ M\ s^{-1}$. The presence of the methyl group might decrease the rate of ligand exchange as compared with the zirconocene dichloride/zirconocene-d_{10} dichloride system.

A possible mechanism has been proposed for the photoexchange reactions [9]. The zirconocene dichloride molecule is a wedge-like sandwich with non-parallel rings (by bending the ferrocene system from D_{5d}, to C_{2v} symmetry). Zirconium is in the +4 oxidation state and has a d^0 electronic configuration in zirconocene dichloride. The location of Cp_2M orbitals can be suggested as in Fig. 1 [10,11].

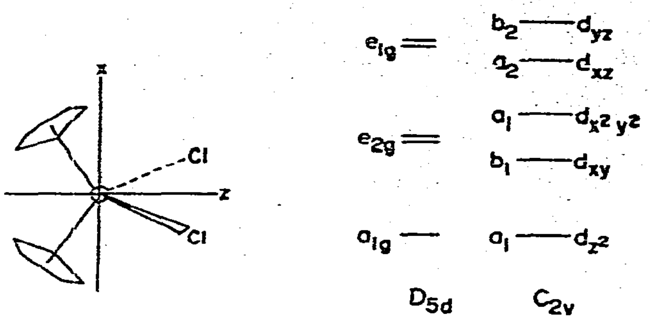
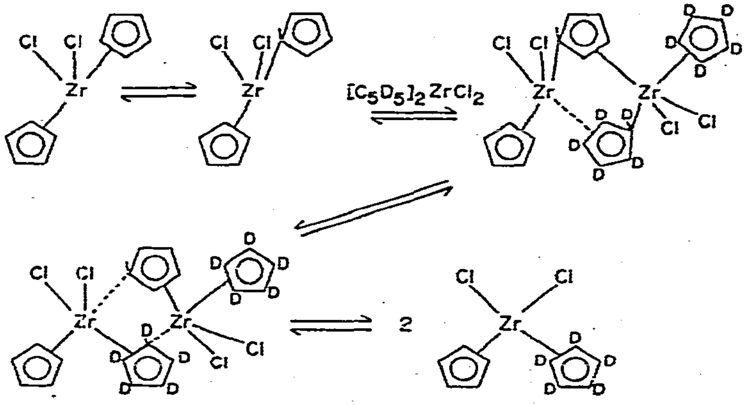


Fig. 1. Zirconzene dichloride and Cp_2M orbitals.



The UV-visible absorption spectrum of zirconocene dichloride in benzene solution showed one strong band centered at λ 295 nm (ϵ_{max} ca. 4500) with a weak band at 335 nm (ϵ_{max} ca. 1100), which probably arises from a ligand to b_2 and $1a_1$ charge-transfer transitions, respectively. It is these transitions which result from irradiation with the 313 nm light used in the photolysis experiments.

It is reasonable to propose the reduction in bond order from η^5 to a lower hapticity as the first step in the zirconocene dichloride/zirconocene-d_{10} dichloride ligand exchange. The attack of the entering group is thus allowed, followed by the possible interchange of low hapticity ligands to η^5 to give the exchanged species. These changes are known for the thermal processes on some titanocene species [12,13], and some zirconocene species [14,15—16].

We cannot rule out the possibility of a free $C_5H_5^\bullet$ radical exchange mechanism, but if $CpTiCl_2$ and $C_5H_5^\bullet$ were formed, one would expect to form $CpTiCl_3$. The latter was not observed unless CCl_4 was added, in which case a radical path is suggested. If CBr_4 was used, both $CpTiCl_3$ and $CpTiBrCl_2$ were found.

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