Photolytic Cyclopentadienyl Ligand Exchange in Selected Systems

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Cyclopentadienyl ligands have been exchanged between molecules of metallocene dichlorides (M = V and Hf) in benzene by photochemical processes. The exchange of cyclopentadienyl ligands between molecules of vanadocene monochloride (or vanadocene) occurs by both thermal and photochemical processes.

Introduction

The photochemistry of organometallic compounds of early transition metals has received considerable attention. Hunt and Winter [1] and McFarlane and Tindall [2] reported the observation of photoreduction of titanium(IV) alkoxides. Harigan, Hammond, and Gray [3] found that, in benzene, photolytic cleavage of the titanocene dihalides gives $CpTiX_2$ radicals. In halogenated solvents this radical abstracts a halogen atom. In our laboratory, the first photoexchange of cyclopentadienyl rings has been reported for the d^0 system [4]. Irradiation of a benzene solution of titanocene dichloride/(D-10)titanocene dichloride with 313 nm wavelength light produced the exchange of the cyclopentadienyl ligand according to the following reaction:

$$(C_5H_5)_2TiCl_2 + (C_5D_5)_2TiCl_2 \rightleftharpoons 2(C_5H_5)(C_5D_5)TiCl_2$$
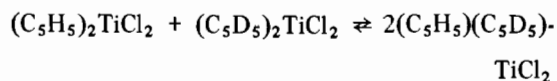
This work was extended to the following metal systems: titanocene monochloride/titanocene-d_{10} monochloride, vanadocene dichloride/bis(methylcyclopentadienyl)vanadium dichloride [5, 6] and zirconocene dichloride/zirconocene-d_{10} dichloride [7].

In the present paper we wish to report cyclopentadienyl ring photoexchanges in the vanadocene dichloride/vanadocene-d_{10} dichloride, vanadocene monochloride/vanadocene-d_{10} monochloride, vanadocene/vanadocene-d_{10}, chromocene/chromocene-d_{10}, and hafnocene dichloride/hafnocene-d_{10} dichloride systems, and some other cyclopentadienyl ring exchange reactions.

Results and Discussion

When benzene solutions containing a vanadocene monochloride/(D-10) vanadocene monochloride mixture were irradiated with 313 nm light (intensity equal to 0.0025 Ei/l-hr), intermolecular exchange of

TABLE I. Mass Spectrographic Data for the Perdeuterovanadocene Monochloride/Vanadocene Monochloride Ligand Exchange.[a]

Time(hr) m/e =	216	221	226	65	66	67	68	69	70	71	I_{221}/I_{226}	F
0	85	1.5	100	85	100	32	20	32	60	58	0.015	0.008
10	90	23	100	90	100	32	16	40	70	64	0.23	0.12
20	92	45	100	81	100	32	21	32	63	57	0.45	0.24
30	89	70	100	78	100	39	24	46	58	70	0.70	0.37
40	90	88	100	82	100	35	20	41	62	66	0.88	0.47
50	94	110	100	84	100	34	18	40	65	62	1.10	0.59
60	92	128	100	85	100	33	19	36	68	64	1.28	0.68
70	87	141	100	87	100	36	20	34	68	66	1.41	0.74
80	90	157	100	82	100	34	18	36	70	65	1.57	0.83
90	88	178	100	86	100	36	17	44	65	60	1.78	0.94
120	91	189	100	82	100	37	18	43	69	64	1.88	1.0

[a]10% thermal-exchange has been substracted from normalized intensity.

the cyclopentadienyl rings occurs. Table I shows the pertinent peaks in the mass spectrum of samples irradiated for varying times. The peak at m/e = 221, corresponding to (D-5) vanadocene monochloride, increases relative to the peaks at m/e = 216 and 226, the D-0 and D-10 species respectively, as photolysis time increases.

The possibility of hydrogen–deuterium exchange rather than cyclopentadienyl exchange is ruled out because there is a constant ratio of all peaks between m/e = 60 and 71 in both photolyzed and unphotolyzed samples. The ratio of the intensities of the m/e = 221 and 216 peaks I_{221}/I_{226} is computed for each irradiation time. The fraction of exchange, F, is calculated on the basis of an equilibrium value of 1.88. For each sample, a plot of ln $(1 - F)$ vs photolysis time was made and the most probable slope was calculated by a standard least squares treatment of the data, and the rate was calculated by using the McKay equation [8]. The quantum yield, calculated by dividing the exchange rate (6.9×10^{-5} M/hr or 1.9×10^{-8} M/sec) by the light intensity (0.0025 Ei l^{-1} hr^{-1}), is 0.028 mol/Ei.

The exchange of cyclopentadienyl ligands is not solely a photochemical process. A 10% thermal exchange is observed when the sample solution is stirred in the dark at room temperature for one week (about 0.5% for every 12 hr). The thermal exchange increases with temperature.

Thermal cyclopentadienyl ligand exchange has also been observed in vanadocene/vanadocene-d$_{10}$ and chromocene/chromocene-d$_{10}$ systems. For vanadocene, this thermal process, which is fast for chromocene, takes a week to reach equilibrium.

Ligand exchange in hafnocene dichloride/hafnocene-d$_{10}$ dichloride occurs only by a photochemical process. The quantum yields (with 313 nm light) for the ligand exchange reactions of the d^0 metallocene dichlorides [4, 7] are all approximately 0.02 mol/Ei.

The cyclopentadienyl ligand exchange in vanadocene dichloride/vanadocene-d$_{10}$ dichloride is also only a photolytic process. The rate of Cp exchange in this system is faster than in bis(cyclopentadienyl)vanadium dichloride/bis(methylcyclopentadienyl)vanadocene dichloride, but slower than in vanadocene monochloride/vanadocene-d$_{10}$ monochloride. The most rapid photolytic Cp exchange was found in the vanadocene/vanadocene-d$_{10}$ system.

More than 20% of the vanadocene dichloride or hafnocene dichloride decomposed photolytically during the 24 hour photolysis at 313 nm required to reach exchange equilibrium, as shown by pmr and optical spectroscopy.

The exchange of the cyclopentadienyl ligand in the three possible binary combinations of Cp$_2$V, Cp$_2$VCl, and Cp$_2$VCl$_2$ was studied. The results are listed in Table II.

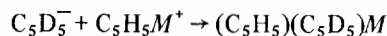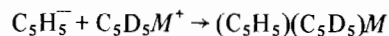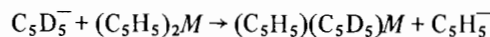TABLE II. Cyclopentadienyl Ligand Exchange between Vanadocene Compounds of Different Oxidation States.
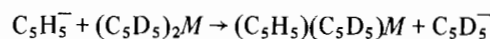
Compounds	Exchange Results	
	(a)	(b)
$(C_5H_5)_2VCl/(CH_3C_5H_4)_2VCl_2$	1%	5%
$(C_5H_5)_2V/(CH_3C_5H_4)_2VCl_2$	3%	30%
$(C_5H_5)_2V/(CH_3C_5H_4)_2VCl$	5%	50%

[a]Room temperature, 24 hours.   [b]70 °C, 24 hours.

Irradiating the reaction mixtures by white light always enhances the reactions and the Cp exchange rates are consistently faster for metals in their lower oxidation states.

The photolytic ring exchange reactions were not detected in the mixed metallocene systems of $(C_5H_5)_2VCl/(CH_3C_5H_4)_2VCl$ or $((C_5H_5)_2TiCl)_2/(CH_3C_5H_4)_2VCl$. The thermal exchange does occur in $(C_5H_5)_2Cr/(CH_3C_5H_4)_2VCl$ and $(C_5H_5)_2Cr/(C_5D_5)_2V$ systems.

Since the ionic nature of chromocene and vanadocene has been demonstrated by studies of conductance [9], the ability to form ferrocene in the reaction of chromocene and vanadocene with ferrous chloride, and the cyclopentadienyl ring exchange involving LiC$_5$D$_5$ and $(C_5H_5)_2M$ (exchange rates decrease in) the order Cr $\gg$ V $\gg$ Fe), the following mechanism for thermal ring exchange may be proposed.

$$(C_5H_5)_2M \rightleftarrows C_5H_5^- + C_5H_5M^+$$

$$(C_5D_5)_2M \rightleftarrows C_5D_5^- + C_5D_5M^+$$

$$C_5H_5^- + (C_5D_5)_2M \rightarrow (C_5H_5)(C_5D_5)M + C_5D_5^-$$

$$C_5D_5^- + (C_5H_5)_2M \rightarrow (C_5H_5)(C_5D_5)M + C_5H_5^-$$

$$C_5H_5^- + C_5D_5M^+ \rightarrow (C_5H_5)(C_5D_5)M$$

$$C_5D_5^- + C_5H_5M^+ \rightarrow (C_5H_5)(C_5D_5)M$$
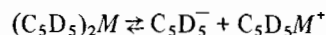
In this scheme each metallocene (M = Cr and V) molecule may form C$_5$H$_5^-$ anion and C$_5$H$_5M^+$ cation, and then through a displacement or recombination reaction, the exchanged species is formed.
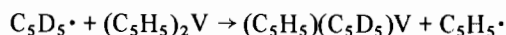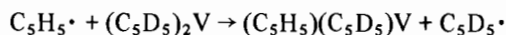
From the postulated mechanism, if the ion dissociation is the rate determining step, we would expect the rate to be directly proportional to the ionicity of the molecule. This expectation is realized in a comparison of exchange rates and conductivity for Cp$_2$Cr, Cp$_2$V and Cp$_2$Fe [9], where the more ionic Cp$_2$Cr also undergoes a more rapid Cp ring exchange than Cp$_2$V, while Cp$_2$Fe (λ = 0) does not undergo ring exchange. We may therefore arrange the compounds in order of decreasing ionicity on the basis of their thermal exchange rates: Cp$_2$Cr > Cp$_2$V $\gg$ Cp$_2$VCl > Cp$_2M$Cl$_2$ (M = V, Ti, Zr, and Hf).

For the photolytic ligand exchange, it is possible that a cyclopentadienide radical is cleaved from the exchanging molecule, as Harrigan, Hammond, and Gray postulated for the titanocene dichloride system. In our laboratory, mass spectrum showed that Cp-TiX$_2$ radical can abstract halogen atoms not only from the halogenated solvent, but also from the titanocene dihalide in the benzene solution. Irradiation of titanocene dichloride/CBr$_4$ (or CH$_3$OH) 1:1 in benzene solutions gives a mixture of CpTiCl$_3$ and CpTiCl$_2$Br (or CpTiCl$_3$ and CpTiCl$_2$(OCH$_3$)) – CpTiCl$_3$ is not expected unless a chlorine atom is abstracted from titanocene dichloride molecule. In the absence of CBr or CH$_3$OH, CpTiCl$_3$ is not found, so it is unlikely that very much CpTiCl$_2$ is formed photochemically without a sensitizer, such as CBr$_3$. Since a radical intermediate is involved in these reactions, and direct photocleavage to generate radicals is important in Cp$_2$VCl$_2$, and Cp$_2$HfCl$_2$ systems (see below), these results justify the following photoinitiated free radical mechanism.
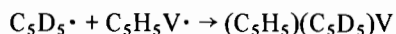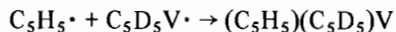
Initiating

$$(C_5H_5)_2V \rightarrow C_5H_5\cdot + C_5H_5V\cdot$$

$$(C_5D_5)_2V \rightarrow C_5D_5\cdot + C_5D_5V\cdot$$

Propagation

$$C_5H_5\cdot + (C_5D_5)_2V \rightarrow (C_5H_5)(C_5D_5)V + C_5D_5\cdot$$

$$C_5D_5\cdot + (C_5H_5)_2V \rightarrow (C_5H_5)(C_5D_5)V + C_5H_5\cdot$$

Termination

$$C_5H_5\cdot + C_5D_5V\cdot \rightarrow (C_5H_5)(C_5D_5)V$$

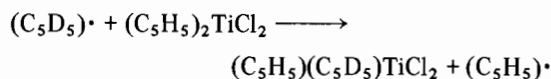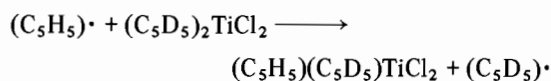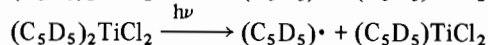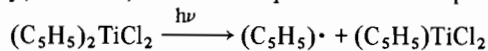$$C_5D_5\cdot + C_5H_5V\cdot \rightarrow (C_5H_5)(C_5D_5)V$$

and other radical recombination process.

There are two possible mechanisms which can be used to explain the photolytic cyclopentadienyl ligand exchange reactions between H-10 and D-10 metallocene dichlorides. First, the bimolecular bridging mechanism which was proposed by Vitz, *et al.* [4–6].
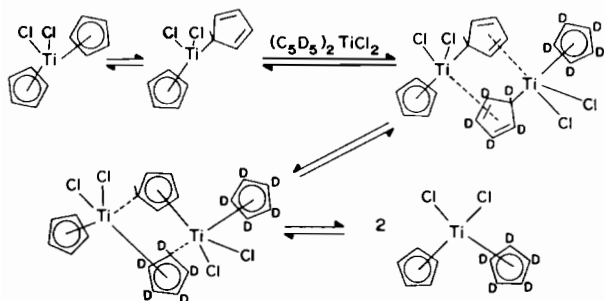
Second, in the photodissociation and recombination mechanism suggested by Harrigan's experiments in benzene, CpTiCl$_2$ can be generated from the direct photocleavage of the Cp$_2$TiCl$_2$ and then rapidly recombine with a cyclopentadiene radical to regenerate

titanocene dichloride, is shown below. In this pathway, however, there is an equal chance for CpTiCl$_2$ to

$$(C_5H_5)_2TiCl_2 \xrightarrow{h\nu} (C_5H_5)\cdot + (C_5H_5)TiCl_2$$

$$(C_5D_5)_2TiCl_2 \xrightarrow{h\nu} (C_5D_5)\cdot + (C_5D_5)TiCl_2$$

$$(C_5H_5)\cdot + (C_5D_5)_2TiCl_2 \longrightarrow$$
$$(C_5H_5)(C_5D_5)TiCl_2 + (C_5D_5)\cdot$$

$$(C_5D_5)\cdot + (C_5H_5)_2TiCl_2 \longrightarrow$$
$$(C_5H_5)(C_5D_5)TiCl_2 + (C_5H_5)\cdot$$

$$(C_5H_5)\cdot + C_5D_5TiCl_2 \xrightarrow{FAST} (C_5H_5)(C_5D_5)TiCl_2$$

$$(C_5D_5)\cdot + C_5H_5TiCl_2 \xrightarrow{FAST} (C_5H_5)(C_5D_5)TiCl_2$$

recombine with a perdeuterocyclopentadiene radical to generate the exchanged species.

As expected, decomposition is usually associated with the Cp exchange process, either by radical abstraction or by radical recombination. Unlike Cp$_2$TiCl$_2$, many bis(cyclopentadienyl) complexes (Cp$_2$VCl$_2$ and Cp$_2$HfCl$_2$) do photodecompose readily in their ring exchange process. These results suggests that the importance of the radical mechanism is greater in these compounds than with Cp$_2$TiCl$_2$.

Experimental

All preparations were carried out under dry argon or in a vacuum and all solvents were refluxed continuously with appropriate drying agents under argon and distilled just before.

D$_2$O was purchased from Mallinckrodt Chemical Works. Metal chlorides (VCl$_3$, VCl$_4$CrCl$_3$, and HfCl$_4$) were purchased from Alfa Products.

Vanadocene, vanadocene monochloride [10], vanadocene dichloride [11], chromocene [12], and hafnocene dichloride [13] were prepared by previously reported methods and their cyclopentadiene-d$_{10}$ and methylcyclopentadiene metallocene analogs similarly.

C$_5$D$_6$ was prepared by the method of Switzer and Rettig [14].

The two filter solutions for the isolation of 313 nm light were: (1) 0.002 M K$_2$CrO$_4$ in 0.07 M K$_2$CO$_3$ (1 cm) and (2) 0.96 M CoSO$_4$ (1.9 cm).

Each benzene solution, containing a metallocene compound (10^{-3} M) and its perdeutero analog (10^{-3} M), was irradiated with 313 nm light in a "merry-go-round" photolysis apparatus. The irradiated samples were analyzed by mass spectrometry (Perkin Elmer RMU-6 Mass Spectrometer). Valerophenone actinomers were used to determine the lamp intensity. These solutions, irradiated under essentially the same condition as the exchange solutions, were analyzed by gas chromatography.

Photolytic Cyclopentadienyl Ligand Exchange between Vanadocene Monochloride and (D-10)Vanadocene Monochloride

Weighed amounts of vanadocene monochloride and perdeuterovanadocene monochloride were stirred with benzene in 50 ml volumetric flasks in a glove box under argon. The solutions were stirred thoroughly and diluted to 200 ml to give 1.1×10^{-2} *M* vanadocene monochloride and 1.2×10^{-2} *M* (D-10)vanadocene monochloride. After mixing the two in dim light, 3.0 ml aliquots were added to the 13 nm culture tubes to make about 60 samples. The tubes were securely stoppered under argon and sealed with an oxypropane torch. Twenty-four exchange samples and six actinomers were mounted in the "merry-go-round" photolysis apparatus equipped with a medium-pressure mercury lamp surrounded by a 313 nm light filter solution. The temperature was maintained at 25 °C. The equipment has been described previously. After measured periods of irradiation, four samples and one actinometer were withdrawn. The samples were pooled, evaporated to dryness, and sublimed at 80 °C before mass spectrometric analysis. The actinometer was analyzed by gas chromatography.

Photolytic Cyclopentadienyl Ligand Exchange between Hafnocene Dichloride and (D-10)Hafnocene Dichloride

The procedure was the same as described above. A mixture of 1.5×10^{-2} *M* hafnocene dichloride and 1.2×10^{-2} *M* (D-10)hafnocene dichloride was used.

Thermal and Photolytic Cyclopentadienyl Ligand Exchange between the H-10 and D-10 Analogues of Cp_2- Cr, Cp_2V and of Cp_2VCl_2

The procedure was the same as described above. The concentration of vanadocene dichloride and its perdeutero analog was 2×10^{-4} *M*. The concentration of vanadocene and its analog was 10^{-2} *M*.

Thermal and Photolytic Cyclopentadienyl Ligand Exchange in the Three Possible Binary Combinations of Cp_2V, Cp_2VCl, and Cp_2VCl_2

Weighed amounts of vanadocene and bis(methyl-cyclopentadienyl)vanadium monochloride were stirred in benzene in 100 ml volumetric flasks in a glove box under argon. The solutions were then mixed thoroughly to give 5.2×10^{-2} *M* vanadocene and 3.7×10^{-2} *M* bis(methylcyclopentadienyl)vanadium monochloride. Half of the solution was stirred in the dark, while the other half was stirred and heated to 70 °C. After 24 hours, the solvent was removed and the samples were analyzed by mass spectrometry.

Similar procedures were used in the study of the $(C_5H_5)_2V/(CH_3C_5H_4)_2VCl_2$ and $(C_5H_5)_2VCl/(CH_3-C_5H_4)_2VCl_2$ systems.

Thermal and Photolytic Cyclopentadienyl Ligand Exchange in the Mixed Metallocene Systems of $(C_5H_5)_2$- $Cr/(C_5D_5)_2V$, $(C_5H_5)_2Cr/(CH_3C_5H_4)_2VCl$, and $(CH_3-C_5H_4)_2VCl/((C_5H_5)_2TiCl)_2$

The procedure was the same as described above.

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