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**Preliminary communication**

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# PHOTOEXCHANGE OF $\eta^5$-CYCLOPENTADIENIDE LIGANDS IN SELECTED SYSTEMS

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## Summary

Cyclopentadienide ligands are exchanged between molecules of di-$\eta^5$-cyclopentadienyltitanium monochloride in benzene, and between bis-(methyl-$\eta^5$-cyclopentadienyl)vanadium dichloride and di-$\eta^5$-cyclopentadienylvanadium dichloride in benzene by a photochemical process. A small amount of dimer is produced upon photolysis of benzene solutions containing both 1,1′-trimethylene titanocene dichloride and titanocene dichloride.

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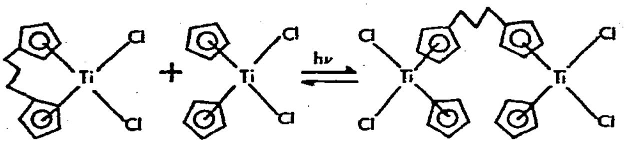
In a previous communication [1], we reported the cyclopentadienide photoexchange in the $d^0$ system, titanocene dichloride/titanocene-$d_{10}$ dichloride. In the present paper we wish to report our findings on the exchange systems with $d^1$ metal ions involving dicyclopentadienylvanadium dichloride/bis(methylcyclopentadienyl)vanadium dichloride, and titanocene monochloride/titanocene-$d_{10}$ monochloride. These systems demonstrate, first, the effect of the single $d$ electron (absent in titanocene dichloride) and second, the effect of involving the halogen ligands in bridging (in titanocene monochloride dimer). We also wish to report our findings on the photolysis of solutions containing titanocene dichloride and trimethylenetitanocene dichloride. Ligand exchange in this system can lead to bridged ferrocenophane-like systems, the simplest of which is dimer I.

When benzene solutions containing titanocene monochloride dimer and titanocene-$d_{10}$ monochloride dimer are exposed to 313 nm irradiation, exchange of the cyclopentadienide ligand between the two molecules occurs. Exchange is demonstrated by converting the photolyzed monochloride to dichloride with chloroform, and obtaining the mass spectrum of the dichloride. As photolysis time increases, the peak at $m/e$ 253, corresponding to $Cp_2TiCl_2{}^+$-$d_5$, increases compared with the peaks at $m/e$ 258 and 248, corresponding to the $d_0$ and $d_{10}$ species. The rate of approach to equilibrium is measured and the data subjected to a standard McKay analysis as reported



(I)

previously [1]. With identical lamp intensity, the titanium monochloride system exchanges cyclopentadienyl ligands at a rate about three times that of the titanocene dichloride system. The titanocene monochloride ligand exchange must lead to $d_5$, $d_{10}$, $d_{15}$ species in addition to the initially present $d_0$ and $d_{20}$ species. The entropy change for this reaction must therefore be much greater than for the titanocene dichloride exchange. The experimental procedure, unfortunately, obfuscates the identity of the species present in the equilibrium mixture, and we can report only the equilibrium constant expressed in terms of the intensities of the measured titanocene dichloride peaks, $K = I^2_{(253)}/I_{(248)} \times I_{(258)} = 4$. Titanocene monochloride dimer and the $d_{20}$ analog were prepared by the method of Coutts et al. [2] in which titanocene dichloride, or titanocene-$d_{10}$ dichloride, was reduced with activated aluminum. The product was washed thoroughly with diethyl ether to remove aluminum chloride. Aluminum chloride, if present, could interfere in the exchange process, but neutron activation analysis demonstrates that aluminum is not present in the product at the sensitivity limit of the method, which detects about 0.1 atom of Al per Ti atom. Perdeuterotitanocene dichloride was prepared as reported previously [1].

It is surprising to find that the cyclopentadienyl ligand exchange proceeds readily even when the halogen ligands are involved in bridging between titanium atoms. The thermal lability of the halogen in titanocene dichloride [1] is apparently not crucial (as a coordination-sphere reducing step) in the mechanism of the exchange. It is possible that a cyclopentadienide radical is cleaved from the exchanging molecule, as Harrigan, Hammond and Gray postulate [3] for the titanocene dichloride system. We have, however, been unable to detect any significant decrease in titanocene dichloride concentrations even after extensive photolysis of titanocene dichloride in benzene at all wavelengths at which the exchange occurs (313, 400 and 520 nm). Thus the observations of Harrigan et al. [3] may be attributable to side reactions with impurities rather than the formation of $CpTiCl_2$ that they claim. We did observe side reactions when all materials were not ultrapure. It is interesting to note that many dicyclopentadienyl complexes, including $Cp_2TaCl_2$, $Cp_2ZrCl_2$, and $Cp_2VCl_2$ do photodecompose readily. We are currently devising experiments to clarify the importance of the other ligands in the cyclopentadienide exchange process in the titanium system.

When solutions containing both vanadocene dichloride and bis(methylcyclopentadienyl)vanadium dichloride are irradiated with 313 nm light, cyclopentadienide exchange occurs according to equation 1. The peak in the

$$(MeCp)_2VCl_2 + Cp_2VCl_2 \xrightleftharpoons{h\nu} 2(MeCp)CpVCl_2 \qquad (1)$$

photolyte mass spectrum at $m/e$ 230 (corresponding to $(MeCp)CpVCl^+$) increases relative to those at *m/e* 244 and 216 (corresponding to $(\mathrm{MeCp})_2\mathrm{VCl}^+$ and $\mathrm{Cp}_2\mathrm{VCl}^+$, respectively) as the photolysis proceeds. The greatest equilibrium quotient measured for this reaction, as calculated from the peak intensities, $K = I^2_{(230)}/I_{(244)} \times I_{(216)}$, is only 1.8. The rate of cyclopentadienide exchange is only about one tenth of that for the titanocene dichloride system. These low figures reflect the importance of side reactions, including photodecomposition. The absorbance of the exchange solution at 385 nm due to $\mathrm{Cp}_2\mathrm{VCl}_2$ is decreased by 34% in the 24 h photolysis at 313 nm required to reach exchange equilibrium. Furthermore, the shoulder at 420 nm in the spectrum of the unphotolyzed samples decreases upon photolysis, and the maximum shifts to about 375 nm. The presence of the methyl group also decreases the rate of ligand exchange. Exchange in the bis(methylcyclopentadienyl)titanium dichloride/titanocene dichloride system occurs only about 0.4 times as fast (with equal absorbed light) as in the titanocene dichloride/titanocene-$d_{10}$ dichloride system. Vanadocene dichloride was found to exchange cyclopentadienide ligands photolytically with titanocene-$d_{10}$ dichloride, but no quantitative data have yet been obtained.

When benzene solutions containing both 1,1′-trimethylenetitanocene dichloride [4] and titanocene dichloride are photolyzed, a very small amount of dimer I is formed. While cyclopentadienide is exchanged between molecules of $10^{-3}$ *M* titanocene dichloride in benzene with a half life of a few hours, only a few percent of the total titanium is present as dimer after photolysis of the mixture for one week. A peak cluster of very low intensity is detected at *m/e* 501±2 in the mass spectrum of photolyzed mixtures from which the benzene was evaporated and the unreacted monomers were sublimed. This peak cluster does not appear in the mass spectrum of unphotolyzed mixtures, and the relative intensities of the peaks are those expected for a species containing 3 chlorine atoms. The most reasonable assignment for this peak is the molecular ion of I minus one chlorine atom. We have been unable to observe a peak corresponding to the dimer of 1,1′-trimethylenetitanocene dichloride.

We expect that polymers may be obtained in larger quantities by photolysis of a well chosen bridged-cyclopentadienyl complex, and that they may possess very interesting catalytic properties.

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