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Preliminary communcation

PHOTOCHEMICAL REACTIONS OF DI-π-CYCLOPENTADIENYL-TITANIUM DICHLORIDE

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Summary

Exchange of cyclopentadienyl ligands between molecules of titanocene dichloride in benzene solutions and alcoholysis of titanocene dichloride in methanol—benzene solutions occur exclusively by photochemical processes. The exchange of cyclopentadienyl ligands between titanocene dichloride and the titanocene monochloride dimer also occurs solely by a photochemical process.

We have been unable to encounter any reports of the exchange of π-bonded cyclopentadienyl ligands between identical transition metal complexes [1,2]. Nor have we found any reports of photochemical studies of titanocene dichloride, Cp_2TiCl_2 [3,4], even though reactions of Cp_2TiCl_2 that involve photochemical pathways have been examined [5] and the compound is an important component of many catalyst systems.

We wish to report results of our study of the photolytic ligand exchange between $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5D_5)_2TiCl_2$ and the methanolysis of Cp_2TiCl_2.

Benzene solutions initially 10^{-2} to 10^{-4} molar in both perdeuterotitanocene dichloride and titanocene dichloride show increasing concentrations of titanocene-d_5 dichloride when subjected to 313 nm light. The equilibrium constant for reaction 1 is equal to the theoretically predicted [6] value of 4

$$(\pi\text{-}C_5D_5)_2TiCl_2 + (\pi\text{-}C_5H_5)_2TiCl_2 \rightleftharpoons 2(\pi\text{-}C_5H_5)(\pi\text{-}C_5D_5)TiCl_2 \qquad (1)$$

within the limits of experimental error, and the quantum yield for ligand exchange is 0.22 when the total titanocene dichloride concentration is 8.2×10^{-3} *M*. Perdeuterotitanocene dichloride was prepared by stirring $(Cp_2TiH)_x$ in toluene under deuterium gas [7], then cooling to —70°C and adding HCl gas. The product was purified by recrystallization from $CHCl_3$ saturated with HCl followed by vacuum sublimation at 130°C. The exchange was monitored by obtaining the mass spectrum of the product mixture after evaporating the photolyzed solutions. The increase in the peak at *m/e* 253 relative to the peaks at 258 and 248 was used as the basis for a standard McKay analysis [8]. The position of equilibrium was obtained by photolyzing the solution for a period of about 40 h (ten times that required to give constant peak ratios). Exchange solutions and valerophenone actinometer solutions were degassed and sealed in 13 mm o.d. pyrex culture tubes and mounted in a merry-go-round apparatus to assure uniform illumination of all samples by the Hanovia medium pressure 450 Watt mercury lamp (679A0360). The convenient 313 nm line was isolated by using a filter solution of 0.002 molar potassium chromate in 1% aqueous potassium carbonate. It was selected because the complex absorbs strongly ($\epsilon > 10^3$) at that wavelength. Further experimental details have been reported previously [9]. Samples were not individually stirred, and some error in the quantum yield may have resulted. 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 72 in both photolyzed and unphotolyzed samples.

Quantum yields were calculated from the rate derived from the McKay equation and the "intensity" of the light in Einsteins per unit time.

Exchange of cyclopentadienyl ligands between perdeuterotitanocene dichloride and titanocene monochloride dimer in benzene solution has been proven by a similar method, except that the titanocene monochloride was removed from the photolyte solutions by precipitation with 2,2′-bipyridine [10] before the mass spectrum of the titanocene dichloride was obtained. The reaction was surprisingly efficient, reaching completion in less than 20 minutes when the concentration of each complex is 10^{-3} *M*.

The alcoholysis of titanocene dichloride is exclusively photolytic, being slow even in boiling ethanol under room illumination [5]. The photolytic methanolysis of titanocene dichloride in benzene solutions was followed by monitoring the decrease of the absorption band of titanocene dichloride at 520 nm, after varying periods of illumination in the apparatus described above. The quantum yield was 0.44 for solutions 8.1×10^{-3} *M* in titanocene dichloride and 1.0 *M* in methanol, and decreased with decreasing concentrations of either reactant.

The photolysis product was isolated by evaporating the solution to dryness and extracting with petroleum ether, which yields yellow crystals on cooling. The product melts at about 100°C, as would be expected for $Cp(OMe)TiCl_2$, since the reported melting point of $Cp(OEt)TiCl_2$ is 48-49°C [5,11] and the boiling point of $Cp(OC_3H_7)TiCl_2$ at 2 mm pressure is 159°C [12]. If the halogens are replaced by alkoxy groups in these complexes, colorless liquids generally result [12].

The mass spectrum of the methanolysis product shows a parent ion peak manifold centered at *m/e* 214, which corresponds to $Cp(OMe)TiCl_2^+$. The relative peak intensities are close to those expected for a species containing 2 chlorine atoms [13]. The spectrum is otherwise predictable [14] except for the absence of a peak at *m/e* 183. The most intense of the large fragment peaks is at *m/e* 148, and the surrounding manifold reflects a high abundance of both $CpTiCl^+$ and $(OMe)TiCl_2^+$ (*m/e* 149).

In light of the above results, we suspected that photolysis might play a role in reactions that do not involve the cyclopentadienyl ligand. Accordingly, we studied the halide exchange between titanocene dichloride and titanocene dibromide, and the electron exchange between titanocene dichloride and titanocene monochloride. Both reactions, however, are complete in the time of mixing and quenching (ca. 1 minute), and apparently proceed by low energy thermal pathways. The equilibrium constant for reaction 2 was determined to be 1.5 from the ratio of the *m/e* 338, 294 and 248 peaks in the mass spectrum.

$$(\pi\text{-Cp})_2\text{TiCl}_2 + (\pi\text{-Cp})_2\text{TiBr}_2 \rightleftharpoons 2(\pi\text{-Cp})_2\text{TiBrCl} \qquad (2)$$

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