

PRELIMINARY NOTE

The preparation and some properties of tris(pyridine)aryl(or alkyl)titanium(III) chloride

Many organotitanium compounds which contain a σ type carbon-titanium bond have been reported¹⁻⁶. However, most of them are unstable and thus not convenient for investigations of the nature of the carbon-titanium bond. It is known that coordination of appropriate ligands can stabilize carbon-transition metal bonds and so we attempted to prepare some organotitanium compounds containing monodentate ligands.

To a pyridine solution of TiCl_3 was added an equimolar amount of dilute ethereal solution of RMgBr ($\text{R} = \text{CH}_3$ or C_6H_5) under nitrogen at -30°C , and the precipitate obtained was dissolved in tetrahydrofuran. After removal of magnesium halide by addition of pentane, the solution was concentrated under reduced pressure to give a deep blue deposit. Elemental and functional group analyses showed that it was $\text{RTiCl}_2(\text{pyridine})_3$ ($\text{R} = \text{CH}_3$ or C_6H_5). These compounds were fairly stable under nitrogen at room temperature but decomposed easily when exposed to the air.

Other alkyl and *para*-substituted-phenyl magnesium bromides also gave deep blue compounds. Aryl derivatives were generally more stable than alkyl derivatives, most of which decomposed rapidly at room temperature, giving R^\cdot radicals.

Each of these compounds showed a broad absorption in 600–800 $\text{m}\mu$ region. For all *para*-substituted-phenyl derivatives, the λ_{max} shifted to longer wave length relative to that of $\text{TiCl}_3(\text{pyridine})_3$ (605 $\text{m}\mu$)⁷ and a good linear correlation was observed between the λ_{max} and the Hammett's σ_p value of the substituent (λ_{max} is 622 $\text{m}\mu$ for Cl -, 660 $\text{m}\mu$ for H -, 662 $\text{m}\mu$ for $\text{C}_6\text{H}_5\text{O}$ -, 675 $\text{m}\mu$ for CH_3 - and 680 $\text{m}\mu$ for CH_3 -compounds.)

Hence, we can conclude that the ligand field strength of the *para*-substituted phenyl group is weaker than that of the Cl^- ion and that its strength decreases as the σ_p value of the substituent lowers. The absorption in the visible region can be assigned to the $\pi^*-\sigma^*$ transition⁷. Hence, it is reasonable that the λ_{max} correlates fairly well with σ_p since the substituent affects not only the π -electron systems but also the σ -electron systems, and σ_p is an empirical index of these effects.

Each of the mixture solutions of TiCl_3 -pyridine- RMgBr showed a fairly symmetrical single ESR absorption with g value close to 2 (1.96–1.98) even at rigid state below -100°C . At higher temperature (above -30°C) the ESR spectra became sharp ($\Delta H < 20$ gauss) and symmetrical, owing to motional narrowing and averaging out of the anisotropy of g value⁸.

Different from the λ_{max} , the correlation between the g value and the σ_p is poor. The constant σ_p can be separated into the inductive (σ') and resonance ($\sigma_{\text{R}} = \sigma_p - \sigma'$) factors⁹. The \bar{g} value (observed at room temperature) shows a fairly good linear correlation with σ_{R} , except for deviation of the $\text{C}_6\text{H}_5\text{O}$ -compound, (\bar{g} is 1.970 for H -, 1.968 for CH_3 -, 1.965 for Cl -, 1.966 for $\text{C}_6\text{H}_5\text{O}$ - and 1.960 for CH_3O -compounds.)

In the ground state of $\text{RTiCl}_2(\text{pyridine})_3$, the unpaired electron would be

principally in π^* -orbitals as in most nearly octahedral complexes of Ti^{3+} ion¹⁰. Therefore, the properties of the unpaired electron would be much more sensitive to π -interaction between titanium and coordinating molecules than to the nature of σ bonds between them. Hence, it would be likely that the \bar{g} value would correlate reasonably well with σ_R , which refers principally to the effects of a substituent on the nature of π -electron systems¹¹, rather than with σ_p .

The \bar{g} value of alkyl derivatives was less affected by the species of alkyl groups as compared with aryl derivatives, and a fairly good correlation was observed between the \bar{g} value and the Taft's σ^* . The effects of the species of alkyl groups on the \bar{g} value were more remarkable when titanium bromide was used instead of chloride.

Details of results and discussions will be presented in the near future.

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