Nature of Cis-Effects in \( \text{mer-Ru(CO)}_3(L)(\text{SiCl}_3)_2 \) Compounds where L is a Phosphorus Donor Ligand

Introduction

It has been found that the rate of substitution of the equatorial carbonyl by \( \text{P(OMe)}_3 \) varies depending on the phosphorus donor ligand in the coordination complex \( \text{mer-Ru(CO)}_3(L)(\text{SiCl}_3)_2 \) where the \( \text{SiCl}_3 \) ligands are cis and L is the phosphorus donor ligand. Unlike trans effects, cis effects are not well documented in textbooks. Consequently, none of the three textbooks for class discuss this effect. The study to be presented is a probe into the nature of this cis effect, alluding to the major contribution to the cis effect in 24 compounds where only the phosphorus donor ligand is varied.

Method

The reaction studied follows the general form of \( \text{Ru(CO)}_3(L)(\text{SiCl}_3)_2 + \text{P(OMe)}_3 \rightarrow \text{Ru(CO)}_2(L)\text{P(OMe)}_3(\text{SiCl}_3)_2 + \text{CO} \) where L is a phosphorus donor ligand\(^2\). For this study to be valid, this reaction must follow the dissociative mechanism. NMR studies were performed to confirm this\(^1\). The equatorial CO group was replaced with \(^{13}\text{CO} \) and mixed with the unmarked compound. NMR spectra were then taken over time to determine whether there was mixing present.
Cone angles and Tolman electronic parameters were compared with the kinetic data in order to determine the degree of influence these factors had on the reaction rate. Cone angles\(^3\) and Tolman electronic\(^4\) parameters were obtained from additional studies.

**Results and Analysis**

The NMR data obtained\(^1\) is indicative of a true dissociative mechanism. Peak A corresponds to the splitting between the \(^{13}\)C and phosphorus in the marked compound while peak B is the result of the phosphorus ligand in the unmarked compound. As time proceeded, mixing occurred between the two peaks until they were roughly equivalent. The central feature indicated no \(^{13}\)C present while the two side peaks indicated the compound with the \(^{13}\)C. This even mixing shows that the equatorially substituted \(^{13}\)C was free to leave and re-associate at random, indicating a true dissociative mechanism with a trigonal-bipyramidal intermediate configuration rather than a seven coordinate associative mechanism.
The compilation of kinetic, electronic, and cone angle data is shown to the right. This data set only includes 20 of the 24 selected phosphorous donor ligands due to complications in the intended reaction. There is essentially no correlation between the electronic parameters and the entropy of activation, indicating that this has limited or no influence on the cis-effect caused by the ligand. The correlation between the cone angle and $\Delta S^\neq$ is significant at $R = 0.94$, agreeing with the value reported by Chalk and Pomeroy in their paper.

When comparing the chart in their paper and the chart I made in Microsoft Excel, all data points are accounted for and correlation coefficients match up.

While the data exhibits this significant correlation, there were four exceptions that were excluded when creating these graphs. These ligands...
are P(OPh)$_3$, P(O-p-MeC$_6$H$_4$)$_3$, P(CH$_2$Ph)$_3$, and PPh$_2$(o-MeOC$_6$H$_4$). These four ligands had $\Delta S^\circ$ values that were close to zero or negative, indicating that other factors are affecting the reaction in these compounds. All these exceptions have secondary donor sites and it is possible that this donor site stabilizes the five coordinate intermediate. Additional NMR studies could be performed to confirm the creation of this proposed five-coordinate intermediate.

**Conclusion**

Through the use of NMR spectroscopy it has been shown that the studied reaction follows the classic dissociative pathway. As the phosphorous donor ligand L was varied, a strong correlation was found between $\Delta S^\circ$ and the cone angle of L. There was also negligible correlation between the electronic parameters and $\Delta S^\circ$. The exhibited cis-effect in these Ru coordination compounds is primarily due to steric hindrance from the phosphorus donor ligand’s cone angle.

**Sources**


