During the course of an investigation seeking to explore the reactivity between dichlorotris(triphenylphosphine)ruthenium(II), RuCl$_2$(PPh$_3$)$_3$, and a series of hydrazines, an unexpected crystallographic result led to an impromptu research project. In addition to the variable, albeit standard, coordination behavior of hydrazines, the reaction between RuCl$_2$(PPh$_3$)$_3$ and 1,2-diphenylhydrazine (hydrazobenzene) resulted in the molecular rearrangement and coordination of ortho-semidine. The transformation of 1,2-diphenylhydrazine to ortho-semidine is commonly referenced as part of the “benzidine rearrangement” family, first reported over 150 years ago. Although this arena has been extensively studied, the rearrangement mediated by RuCl$_2$(PPh$_3$)$_3$ is only the third report that involves a transition metal complex. The molecular structure of this product, RuCl$_2$(PPh$_3$)$_2$(κ$^2$-NH$_2$-1,2-C$_6$H$_4$-NHPh), which has one chiral nitrogen center, was conclusively elucidated by single-crystal X-ray diffraction where spectroscopic analysis was ambiguous. Two polymorphs were obtained, one chiral ($P2_12_12_1$) and one centrosymmetric ($P2_1/n$). The former is the dominant form, while the latter is considered “disappearing”. Phase purity of the dominant form was confirmed by powder X-ray diffraction. Interestingly, the product undergoes spontaneous resolution to produce this polymorph. Across three different laboratories, the “disappearing” polymorph could not be obtained again. The crystallographic and structural analyses of this saga will be discussed.

*Figure 1*