

Activation of the pentamethylcyclopentadienyl group bound to nickel group metals towards Diels–Alder addition

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Cyclopentadienyl complexes of the type $[M(\eta^5\text{-C}_5\text{R}_5)\text{L}_2]$ ($M = \text{Co, Rh, Ir, Ni}$; $L = 2e^-$ or $1e^-$ donor) are well-known to exhibit two types of distortion arising from loss of degeneracy of the e orbitals of the cyclopentadienyl group on interaction with the frontier orbitals of the ML_2 fragment¹.

We have studied this distortion in pentamethylcyclopentadienyl complexes of platinum and have found that neutral systems of the type $[(\eta^5\text{-C}_5\text{Me}_5)\text{PtLX}]$ ($L = \text{CO, PR}_3$; $X = \text{halide, alkyl}$) where the distortion is large, the pentamethylcyclopentadienyl ring is activated towards the Diels–Alder addition of a variety of dienophiles including dioxygen and we are able to isolate complexes containing the bound adduct. This process is inherently face-selective. We describe the effect of metal ligand substitution on the *syn/anti*-isomer ratio of the complexes produced. All these complexes were characterized by various spectroscopic techniques. In addition, complexes of dioxygen adduct and ethyl vinyl ketone adduct were characterized by single crystal X-ray crystallography.

Reference

1. Lichtenberger D L, Blevins II C H and Ortega R B 1984 *Organometallics* **3** 1614