Characteristics of Indenyl Systems

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Kinetic experiments are fundamental in the elucidation of the mechanisms involved in ligand substitution reactions and in the determination of what factors contribute to the rates of these reactions. Such experiments were essential in determining the mechanism for CO substitution in η^5-indenyl metal carbonyl complexes.

The introduction of benzo substituent onto a cyclopentadienyl system results in an indenyl group and has profound effects on the properties of the five-membered ring when it functions as a π-bonded ligand to a transition metal. In particular, the η^5 to η^3 transformation is made much easier. This is known as the indenyl effect [1]. Over the last two decades the kinetics and mechanisms of carbon monoxide substitution reactions of η^5- indenyl metal carbonyl complexes have been studied in detail [2]. The reactions are known to take place by an associative process, of which the intermediate is proposed to be an η^3-bound indenyl group attached to a metal center which is attacked by the incoming nucleophile. The $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage mechanism maintains an 18-electron count around the metal center, thus avoiding an energetically unfavorable 20-electron intermediate.

Indenyl metal complexes, i.e. $(\eta^5\text{-}C_9H_7)ML_n$, are thus found to be more reactive than the corresponding cyclopentadienyl metal complexes in ligand substitution reactions due to an easier ring slippage of the bound indenyl ring. The re-aromatization of the benzene ring of the indenyl group in the 18-electron intermediate is thought to drive this associative reaction [2c]. A relative rate increase of 10^8 was observed for carbon monoxide substitution by phosphines in $(\eta^5\text{-}C_9H_7)Rh(CO)_2$ over $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ [2b]. Substituent groups on the indenyl ring can increase or decrease the rate of CO substitution [3a] as well as the replacement of a carbon atom of the indenyl ring with a more electronegative nitrogen atom [3b,c]. One of the first isolated η^3-indenyl complexes was that of $(\eta^3\text{-}C_9H_7)Ir(PPhMe_2)_3)$ [4].

Recently there has been increased emphasis on determining the relationship of the structure of these indenyl complexes to their ability to undergo facile ring slippage in order to improve the design of catalytic systems [5]. In the solid state some η^5-indenyl complexes exhibit pronounced distortions to η^3 bonding with the fused benzene ring folding away from the allylic fragment and the metal center slipping towards carbon 2, as exemplified by $[(\eta^5\text{-}C_9H_7)Ir[P(C_6H_5)_3]_2H]BF_4$ [6]. The degree of this distortion to a η^3-bonding or slip-folding is expressed in three parameters: the slip distortion ΔMC (distance toward C_2), the fold angle Ω (folding away of benzene ring), and the hinge angle α [6a]. Todd Marder and co-workers have developed a measure of the amount of slip folding based on X-ray crystallographic data of substituted indenyl complexes and have related this slip-fold distortion to the σ-donor/π-acceptor characteristics of these ligands [5a]. The larger the value of ΔMC, Ω, and α the more distortion of an η^5-indenyl ligand and the better the σ-donating ability of the other ligands. In solution this degree of slip-fold distortion can be correlated to the downfield or upfield ^{13}C NMR shifts of the indenyl ring juncture carbons [7].
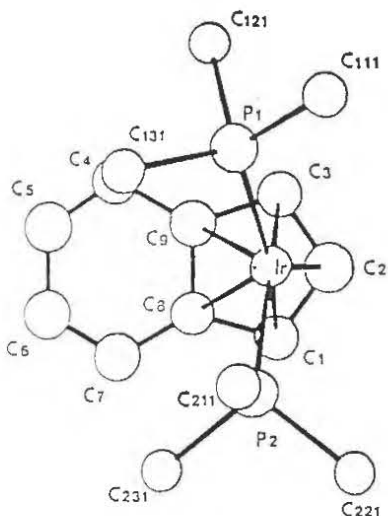
$\Delta MC = 0.20\ A$

$\Omega = 5.9°$

$\alpha = 3.5°$

⊕ Centroid of five-member ring

This slip fold distortion in indenyl complexes results in an increase in the energy barrier of ring rotation [5a]. The larger the slip-fold distortion to η^3-bonding the higher is the energy barrier to rotation [5a].

Invoking this ring slippage mechanism in the cyclotrimerization of acetylenes and in other homogeneous catalytic systems one can then understand the higher yields and higher turnover rates of $(\eta^5\text{-}C_9H_7)RhL_2$, where L is a neutral ligand, compared to the corresponding $(\eta^5\text{-}C_5H_5)RhL_2$ complexes [8]. The indenyl complex $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ has just recently been shown to actively catalyze the addition of ethylene to simple aldehydes to give selective ketones in intermolecular hydro-acylation with no significant decarbonylation [5b].

Of recent interest is that the indenyl ligand is thought to be interconverted from $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1 \rightarrow \eta^0$ when $(\eta^4\text{-}1,5\text{-}C_8H_{12})Ir(\eta^5 C_9H_7)$ reacts at room temperature with PMe_3 and the indenyl ligand migrates to the C_8H_{12} ring [9].

In conclusion, there is a growing body of evidence to support a ring slippage mechanism to account for the increased observed substitution rates for indenyl metal complexes. By exploring further the factors that determine these reaction rates one may be able to fine tune these rates for optimum homogeneous catalysis conditions.

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