The Indenyl Ligand Effect on the Rate of Substitution Reactions of $Rh(\eta\text{-}C_9H_7)(CO)_2$ and $Mn(\eta\text{-}C_9H_7)(CO)_3$

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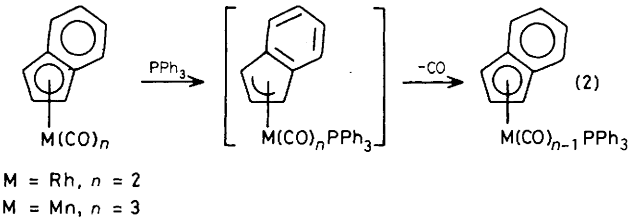
Carbonyl substitution by triphenylphosphine (PPh_3) in the indenyl compounds $Rh(\eta\text{-}C_9H_7)(CO)_2$ and $Mn(\eta\text{-}C_9H_7)(CO)_3$ proceeds by a second order rate law which is first order in complex and first order in PPh_3 and in both cases the rates are much faster than for the corresponding cyclopentadienyl complexes; for rhodium a rate enhancement of 10^8 is found for the indenyl compound over the corresponding cyclopentadienyl compound.

Our interest[1] in the area of organometallic substitution reactions has led us to examine the reactions of several indenyl complexes. In certain cases, cyclopentadiene is a ligand which allows associative substitution[2,3] reactions at 18-electron metal centres. We report here the results of associative substitution of CO by triphenylphosphine (PPh_3) for Mn and Rh compounds where indene has replaced cyclopentadiene.

Studies[4,5] have shown that $Rh(\eta\text{-}C_9H_7)(C_2H_4)_2$ is a very reactive species, substituting both C_2H_4 ligands easily. We have examined[5] the reaction of $Rh(\eta\text{-}C_9H_7)(CO)_2$ with PPh_3 [equation (1)]. The reaction was monitored by measuring the increase in absorbance at 362 nm, which corresponds to λ_{max} for $Rh(\eta\text{-}C_9H_7)(CO)PPh_3$. Under pseudo-first order conditions, the rate of substitution is directly proportional to the concentration of added PPh_3. Thus the reaction proceeds by an associative (S_N2) mechanism, similar to that reported[2] earlier for the analogous cyclopentadienyl compound. The second order rate constant for equation (1) has a value of 2.8×10^4 l mol^{-1} s^{-1}. This is more than 10^8 times faster than the reaction[2] of $Rh(\eta\text{-}C_5H_5)(CO)_2$ with PPh_3 under the same experimental conditions!

$$Rh(\eta\text{-}C_9H_7)(CO)_2 + PPh_3 \xrightarrow[20\ ^\circ C]{toluene} Rh(\eta\text{-}C_9H_7)(CO)PPh_3 + CO \qquad (1)$$

Several studies[6] have shown that indene accelerates a CO dissociation (S_N1) process by two to four orders of magnitude.



(2)

It is significant to note that the rate of reaction for an S_N2 path is 10^8 times faster for indenyl over cyclopentadienyl, suggesting that the indenyl stabilizes the transition state for an S_N2 path more than it does for an S_N1 path relative to cyclopentadiene in these systems.

We also investigated the reactions of $Mn(\eta\text{-}C_9H_7)(CO)_3$,[7] expecting it to react, whilst the corresponding cyclopentadienyl compound is known not to react. Angelici and Loewen[8] report that $Mn(\eta\text{-}C_5H_5)(CO)_3$ shows no reaction after treatment with PPh_3 for three days in decalin at 140 °C. Under these conditions $Mn(\eta\text{-}C_9H_7)(CO)_3$ reacts with PPh_3 to afford $Mn(\eta\text{-}C_9H_7)(CO)_2PPh_3$. The rate of this reaction was followed by monitoring the disappearance of the i.r. carbonyl absorptions of $Mn(\eta\text{-}C_9H_7)(CO)_3$. Only one CO is replaced and the reaction is second order overall, being first order in both $Mn(\eta\text{-}C_9H_7)(CO)_3$ and PPh_3. At 130 °C the second order rate constant is 1.68×10^{-6} l mol^{-1} s^{-1}. This rate of reaction must be at least several orders of magnitude faster than that of the corresponding cyclopentadienyl complex, which does not show a detectable amount of reaction after three days under similar conditions.

These results are consistent with the mechanism proposed[2,3] for associative substitution reactions of cyclopentadienyl complexes. For the indenyl complexes this can be represented by equation (2). This same mechanism was also proposed[5] for the reaction of $Rh(\eta\text{-}C_9H_7)(C_2H_4)_2$ with acetylenes. The tremendous rate enhancement observed for indenyl compounds over cyclopentadienyl compounds has been attributed to the rearomatization of benzene in the transition state, which stabilizes the ene fragment of the allyl–ene transition state. Cyclopentadiene, which has no such stabilization, needs more energy to achieve this transition state.

We have also examined the fluorenyl compound, $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$.[7,9] Upon treatment with PPh_3 a solution of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ in decalin at 130 °C afforded $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2PPh_3$. Kinetic studies of the reaction showed it to be of an S_N2 type, with a second order rate constant of $1.13 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$. This is a 60-fold increase over the rate of reaction of $Mn(\eta\text{-}C_9H_7)(CO)_3$. Thus, the very large rate enhancement in these systems comes from the addition of the first fused benzene ring to the cyclopentadienyl ligand. The enhancement of the rates of associative substitutions decreases by changing the ligand in the order fluorenyl $>$indenyl $>>>$ cyclopentadienyl. This indenyl ligand effect on rates of substitution reactions of transition metal organometallics could be important in their use as homogeneous catalysts, where substitution lability on the catalyst is essential.

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