Relative Reactivity of Co-ordinated Ligands in the Dienyltricarbonyl-ruthenium Cation, $[(\text{dienyl})\text{Ru}(\text{CO})_3]^+$

By R. J. H. COWLES, B. F. G. JOHNSON, P. L. JOSTY, and J. LEWIS*

(*Department of Chemistry, University College, Gower St., London, W.C.*1)

A NUMBER of diene–iron tricarbonyl complexes have been reported.[1] Many undergo hydride ion abstraction with triphenylmethyl tetrafluoroborate to give the cationic derivatives $[(\text{dienyl})\text{Fe(CO)}_3]\text{BF}_4$ (see, *e.g.*, ref. 2). These undergo nucleophilic addition to give substituted diene complexes of the type $(\text{diene Y})\text{Fe(CO)}_3$ (Y^- = nucleophile) (see, *e.g.*, ref. 3). The corresponding chemistry of ruthenium is virtually unexplored.[4] However, it has been demonstrated[5] that the reactivity of co-ordinated ligands such as dienes depends upon the metal, its electronic configuration, and the other ligands present in the complex. It was therefore of interest to prepare and examine complexes of the type $(\text{diene})\text{Ru(CO)}_3$.

The complexes, $C_6H_8\text{Ru(CO)}_3$ and $C_8H_{12}\text{Ru(CO)}_3$, have been prepared from the reaction of dodecacarbonyltriruthenium and a diene, diene = cyclohexa-1,3-diene or cyclo-octa-1,5-diene, in benzene under reflux. The ready formation of a complex with cyclo-octa-1,5-diene is in marked contrast to the behaviour of iron[6] and the complex appears to involve a σ-carbon and a π-allyl mode of bonding. Treatment of these complexes with triphenylmethyl tetrafluoroborate gives the salts $[(C_6H_7)\text{Ru(CO)}_3]\text{BF}_4$ and $[(C_8H_{11})\text{Ru(CO)}_3]\text{BF}_4$ which react with nucleophiles to give as the ultimate product the substituted complexes $(C_6H_4Y)\text{Ru(CO)}_3$ and $(C_8H_{11}Y)\ \text{Ru(CO)}_3$. However, with methoxide ion the initial product is an ester, $[(C_6H_7)\text{Ru(CO)}_2(\text{CO}_2\text{Me})]$ or $[(C_8H_{11})\text{Ru(CO)}_2(\text{CO}_2\text{Me})]$, indicating that the nucleophilic addition occurs in the first instance at a co-ordinated CO group followed by rearrangement to give the substituted complex. Addition of methoxide[7] to co-ordinated carbonyl groups in cationic compounds has been noted previously, but subsequent rearrangements of the type described here have not been reported. The action of acid on $(\text{dienyl})\text{Ru(CO)}_2(\text{CO}_2\text{Me})$ regenerates the cationic derivatives. Similar behaviour has been noted with $\pi\text{-}C_5H_5\text{Fe(CO)}_2(\text{CO}_2\text{Me})$.[8]

A path often suggested for attack by electrophiles on metal complexes involves initial attack on the lone pair of electrons on the metal with subsequent transfer to the co-ordinated ligand. These reactions provide the first examples of attack of a nucleophile at a co-ordinated centre with subsequent transfer to another site within the molecule, although Wilkinson and McCleverty[9] have shown that heating $\text{Mo}(C_5H_5)(\text{CO})_3\text{Et}$ at 100° causes transfer of the ethyl group from the metal to the cyclopentadienyl ring, the main product being $\text{Mo}_2(C_5H_4\text{Et})_2(\text{CO})_6$.

The marked change in the relative reactivity of the ligands present in the dienyl salts $[(\text{dienyl})\text{Fe(CO)}_3{}^+]$ and $[(\text{dienyl})\text{Ru(CO)}_3]^+$ towards nucleophilic attack may be associated with the relative π-bonding capacity of the carbonyl groups and the metal ion, as the reduced electron donation from the metal to the carbonyl groups would enhance the susceptibility of the carbonyl group towards nucleophilic attack. Alternatively, the difference between the iron and ruthenium complexes may relate to differences in kinetic lability of the two systems.

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