CHAPTER SIX

Seven-electron ligands, mixed sandwich complexes, related azulene derivatives and cyclo-octatetraene complexes

Mixed sandwich complexes are those which have two aromatic \(\pi\)-bonded rings containing different numbers of carbon atoms, examples being \(\pi\)-C\(_3\)H\(_5\)Mn-\(\pi\)-C\(_6\)H\(_6\), \([\pi\)-C\(_4\)R\(_4\)Co-\(\pi\)-C\(_6\)R\(_6\)]\(^+\), and \(\pi\)-C\(_2\)H\(_3\)Cr-\(\pi\)-C\(_7\)H\(_7\). The best known 7-electron ligand is the \(\pi\)-C\(_7\)H\(_7\), cycloheptatrienyl group and the preparation and chemistry of its complexes frequently involves mixed sandwich complexes. Thus it is convenient to consider the chemistry of some mixed sandwich complexes in this section, after a discussion of 7-electron ligands.† Since complexes derived from azulene may contain 7-electron ligands and may be mixed sandwich complexes, their chemistry is also considered here. Finally, cyclo-octatetraene and its derivatives may act as ligands in so many ways that their chemistry is discussed at the end of this section, after the related chemistry of 2-, 3-, 4-, 5-, 6- and 7-electron ligands.

A. 7-Electron ligands

(a) Preparation of \(\pi\)-cycloheptatrienyl complexes

Cycloheptatriene metal complexes, where the cycloheptatriene is acting as a 6-electron ligand, may undergo hydride abstraction to give \(\pi\)-cycloheptatrienyl metal cations.

\[
\begin{align*}
\text{Ph}_3\text{C}^+ \text{BF}_4^- & \quad \rightarrow \quad \text{BF}_4^- + \text{Ph}_3\text{CH} \\
& \quad \text{Mo} \quad \text{CO} \quad \text{CO} \quad \text{CO} \\
\text{Mo} \quad \text{CO} \quad \text{CO} \quad \text{CO} \\
\end{align*}
\]

In some cases, the expulsion of a hydrogen atom may occur spontaneously,

† For a review, see reference [1a].

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as shown in the carbonyl displacement reactions,

$$\pi-C_5H_5V(CO)_4 + C_7H_8 \xrightarrow{[3]} \pi-C_7H_7V\pi-C_5H_5$$

$$V(CO)_6 + C_7H_8 \xrightarrow{[4, 5]} \pi-C_7H_7V(CO)_3 + [\pi-C_7H_7VC_7H_8]^+ + V(CO)_6^-$$

and in the displacement of benzene.

$$\pi-C_6H_6Cr \pi-C_6H_6 \xrightarrow{AlCl_3} C_7H_5 \xrightarrow{[8]}$$

The complex 6.1, may also be prepared by the reductive olefination procedure [7, 8, 9], viz.,

$$\pi-C_3H_5CrCl_2.THF + 2 i-C_3H_7MgBr \xrightarrow{Et_2O} \text{[intermediate]} \text{[6.2]}$$

As shown in the above reaction, a hydrogen is removed catalytically from the cycloheptatriene complex, 6.2.

The preparation of $\pi$-cycloheptatrienyl complexes by ring expansion reactions is discussed in section A (c), (i).

(b) Structure

The structures of two $\pi$-cycloheptatrienyl complexes have been determined by X-ray analysis and are given in Figure 45.

Fig. 45. The structures of $\pi$-cyclopentadienyl-$\pi$-cycloheptatrienyl vanadium [10] and $\pi$-cycloheptatrienylvanadium tricarbonyl [11]