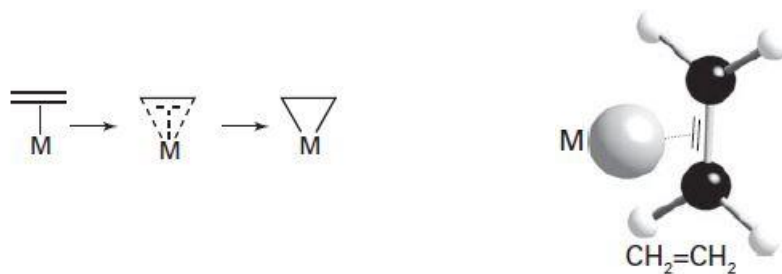


METAL-ALKENE COMPLEXES:

Structure:

Key point: The bonding of an alkene or an alkyne to a metal atom is best described as a σ interaction from the multiple bond to the metal atom, with a π backbonding interaction from the metal atom to the π^* antibonding orbital on the alkene or alkyne.

Alkenes are routinely found bound to metal centres: the first organometallic compound isolated, Zeise's salt, was a complex of ethene. Alkenes normally bond side-on to a metal atom with both carbon atoms of the double bond equidistant from the metal with the other groups on the alkene approximately perpendicular to the plane of the metal atom and the two carbon atoms (31). In this arrangement, the electron density of the C=C π bond can be donated to an empty orbital on the metal atom to form a σ bond. In parallel with this interaction, a filled metal d orbital can donate electron density back to the empty π^* orbitals of the alkene to form a π bond. This description is called the Dewar-Chatt-Duncanson model (**Fig.**) and η^2 -alkenes are considered to be two-electron neutral ligands. Electron donor and acceptor character appear to be fairly evenly balanced in most ethane complexes of the d metals, but the degree of donation and backdonation can be altered by substituents on the metal atom and on the alkene. When the π backbonding from the metal atom increases, the strength of the C=C bond decreases as the electron density is located in the C=C antibonding orbital and the structure tends to that of a C-C singly bonded structure, a metallocyclopropane:



Dihaptoalkenes with only a small degree of electron donation from the metal have their substituents bent slightly away from the metal atom, and the C=C bond length is only slightly greater than in the free alkene (134 pm). When the degree of backdonation is greater, substituents on the alkene are bent away more from the metal atom and the C-C bond length approaches that characteristic of a single bond. Steric constraints can also force the other groups on the alkene to bend away from the metal atom.

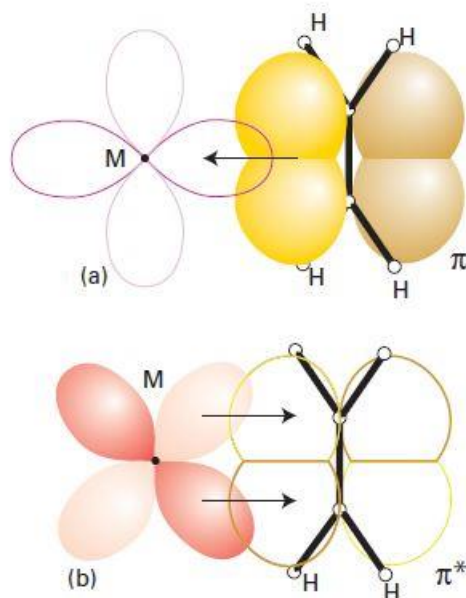
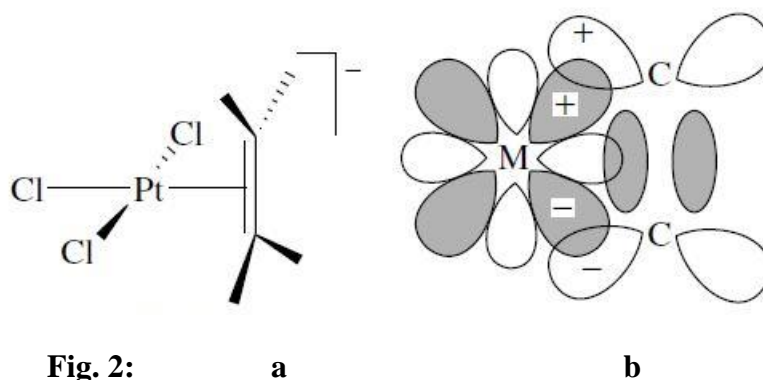


Fig. 1: The interaction of ethane with a metal atom. (a) Donation of electron density from the filled π molecular orbital of ethene to a vacant metal orbital. (b) Acceptance of electron density from a filled d_{π} orbital into the vacant π^* orbital of ethene.

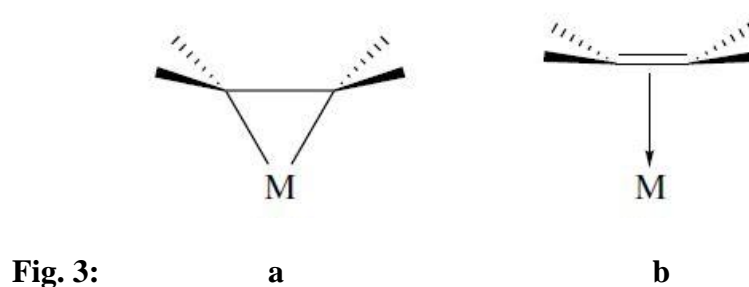
Zeise's Salt:

In 1827, the Danish chemist Zeise obtained a new compound he took to be $\text{KCl} \cdot \text{PtCl}_2 \cdot \text{EtOH}$ from the reaction of K_2PtCl_4 with EtOH. Only in the 1950s was it established that Zeise's salt, **Fig. 2a**, is really $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$, containing a coordinated ethylene, formed by dehydration of the ethanol, and a water of crystallization. The metal is bonded to both carbons of the ethylene, but the four C–H bonds bend slightly away from the metal, as shown in **5.4**; this allows the metal to bind efficiently to the π electrons of the alkene. For Zeise's salt, the best bonding picture is given by the Dewar–Chatt model. This involves donation of the C=C π electrons to an empty d_{σ} orbital on the metal, so this electron pair is now delocalized over three centers: M, C, and C'. This is accompanied by back donation from a metal d_{π} orbital into the ligand LUMO, the C=C π^* level, as shown in **Fig. 2b** (occupied orbitals shaded). By analogy with the bonding in CO, we will refer to the former as the “ σ bond” and the latter as the “ π bond.” As is the case for CO, a σ bond is insufficient for tight binding, and so only metals capable of back donation, and not d^0 metals such as Ti(IV), bind alkenes well. In Zeise's anion, **Fig. 2a**, the metal is located out of the C_2H_4 plane so that it can interact with the alkene π bond. The M–(C_2H_4) σ bond involves donation of the C=C π electrons to an empty M(d_{σ}) orbital, so this electron pair is now delocalized over three centers, M, C, and C'. The M–(C_2H_4) back bond involves donation

from $M(d_\pi)$ to the $C=C \pi^*$ orbital (5.2). As we saw for CO, a σ bond is insufficient for significant M-L binding, and so only d^2-d^{10} metals, capable of back donation, bind alkenes well



The C=C bond of the alkene lengthens on binding. The M-alkene σ bond depletes the C=C π bond by partial transfer of these electrons to the metal and so slightly weakens and, therefore, lengthens it. The major factor in lengthening the C=C bond, however, is the strength of back donation from the metal. By filling the π^* orbital of the C=C group, this back donation can sharply lower the C-C bond order of the coordinated alkene. For a weakly π -basic metal this reduction is slight, but for a good π base it can reduce it almost to a single bond. For Zeise's salt itself, M-L σ bonding predominates because the Pt(II) is weakly π basic, and the ligand (C-C: 1.375 Å), more nearly resembles the free alkene (1.337 Å). The substituents are only slightly bent back away from the metal, and the C-C distance is not greatly lengthened compared to free ethylene. Pt(0), in contrast, is much more strongly π basic, and in $Pt(PPh_3)_2C_2H_4$, the C-C distance becomes much longer (1.43 Å). In such a case the metal alkene system approaches the metalacyclopropane extreme, **Fig. 3a**, as contrasted with the Dewar-Chartt model, **Fig. 3b**, involving minimal π back donation; both are considered η^2 structures.



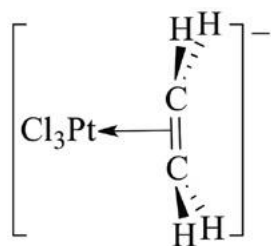
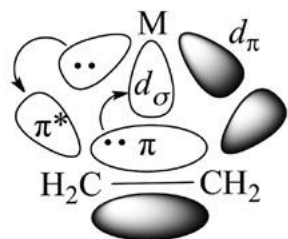
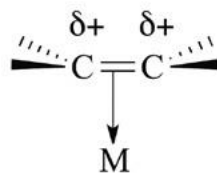


Fig. 2: a

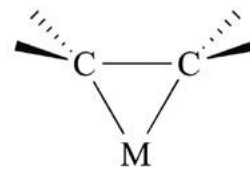


b



Dewar-Chatt

Fig. 3: a



Metalacyclopropane

b

Preparation:

Alkene complexes are often made by displacement of CO or halide ion by an alkene. The formation of Zeise's salt, $KPtCl_3 \eta^2-C_2H_4$ is catalysed by $SnCl_2$ with $PtCl_3 \eta^2-SnCl_3^{2-}$ being the intermediate. The $PtCl_3 \eta^2-C_2H_4$ ion contains a square planar (or pseudo-square planar) Pt(II) centre and in the solid state, the ethene ligand lies perpendicular to the coordination 'square plane', thereby minimizing steric interactions.

