Arene Metal Complexes

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Arenes are aromatic compounds which can act as π-electron donors. Organometallic complexes with such ligands are commonly known as arene complexes, arene metal complexes or metal arene complexes. Arene ruthenium complexes have shown better anticancer activity than the well-known drug cisplatin, *cis*-[$PtCl_2(NH_3)_2$]. Benzene or benzenoid rings are the most common arene ligands. Since these aromatic ligands use their π-systems to bond with metal centers, they are able to show multiple coordination modes which are referred to as the **hapticity.** The most common hapticity is 6 (η^6) with all **six adjacent atoms** in the ring linked to the metal, in addition to hapticities 4 (η^4) and 2 (η^2). We know that benzene undergoes electrophilic substitution reactions. Once an arene ligand coordinates with a metal, the ring becomes more electrophilic (electron-poor), which makes the nucleophilic substitution on the ring more feasible.

Arene complexes are mainly of two categories: **half-sandwich** and **sandwich**. In half-sandwich complexes, [$(C_6H_6)Cr(CO)_3$] (**1a**), the metal is coordinated only to one arene ligand with other ligands such as halides, hydrides, alkyls, carbonyls and phosphines.
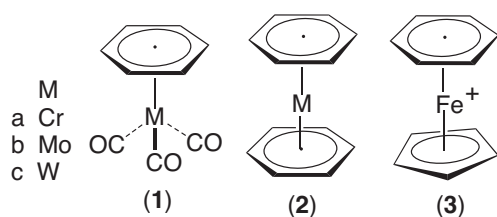

Fig. 1: Piano-stool & sandwich complexes

These complexes with three simple ligands are called **piano-stool** complexes (**1**). When a metal is sandwiched between two arene ligands such complexes are known as **sandwich** complexes, *e.g.* (**2**) and (**3**).

In **homo**-sandwich complexes, [$M(\eta^6\text{-}C_6H_6)_2$] (**2**), both arenes are the same whilst **hetero** complexes, [(η^6-C_6H_6)Fe(η^5-C_5H_5)]$^+$ (**3**), have two different arenes. Arenes show a higher selectivity towards chromium due to its higher stability. Many *d*-elements form arene complexes; some obey the 18-electron rule. Some of the exceptions are [$Ti(C_6H_6)_2$] (16e), [$V(C_6H_6)_2$] (17e) and [($C_6Me_6)_2Fe$] (20e). Examples for 18e half-sandwich complexes or ions include (**1**), [(C_6H_6)$Mn(CO)_3$]$AlCl_4$, [(C_6Me_6)$Fe(CO)_2$], [(C_6H_6)$V(CO)_4$]$^+$ and [(η^4-C_6H_6)Ru(η^6-C_6Me_6)].

Synthesis of arene complexes

The accidental synthesis of the first arene complex took place in early 1919, when Hein mixed Grignard reagent (PhMgX) and $CrCl_3$, but he failed to identify the product as bis(benzene)chromium, [$Cr(\eta^6$-$C_6H_6)_2$].
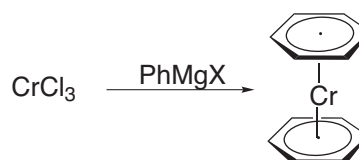

Fig. 2: Hein synthesis of [$Cr(\eta^6$-$C_6H_6)_2$] (**2a**)

A more rational procedure was put forward in 1955 by Fischer and Hafner (Fig. 3). In this procedure, Al powder is a reducing agent and $AlCl_3$ is a catalyst which

can generate $AlCl_4^-$ anion. The 17e Cr(I) salt (**4**), which seems to be quite stable, can be reduced by $Na_2S_2O_8$ to form zerovalent arene Cr(0) complex (**5**). This method is not suitable for arenes with substituents such as halogens or NMe_2 groups which tend to interact with $AlCl_3$.
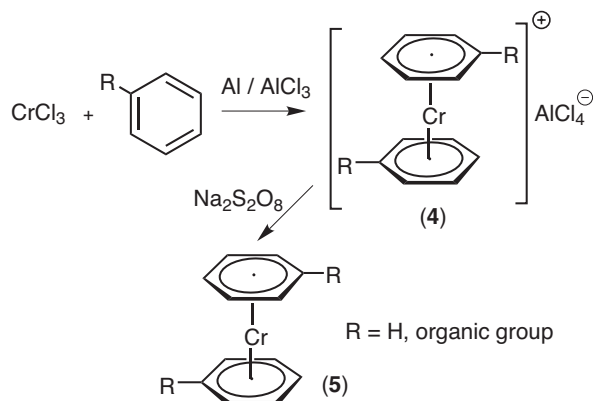

Fig. 3: Fischer-Hafner synthesis

Co-condensation

In this co-condensation method, the vaporized metal and the arene vapor are condensed at very low temperatures to form sandwich and half- sandwich complexes.
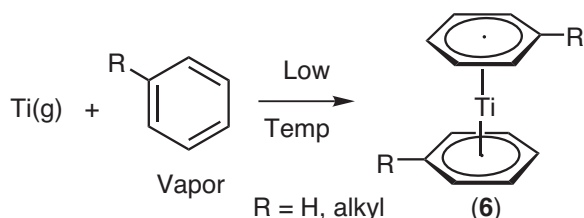

Fig. 4: Synthesis of bis(arene)titanium

This method is even feasible for the preparation of arene complexes with low electron count metals such as Ti, Nb, Y, Gd, Zr, Hf *etc*. Unlike in Fischer synthesis, arenes with reactive lone pairs (*e.g.* chlorobenzene) can be used. Co-condensation technique can also be used to synthesize a wide range of arene complexes, using even sterically strained/demanding arenes as shown below.
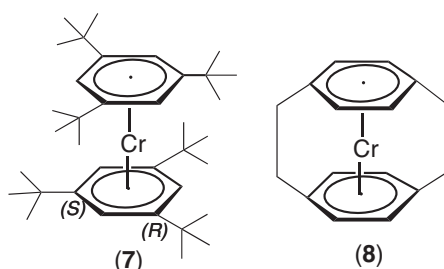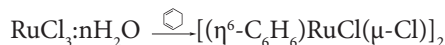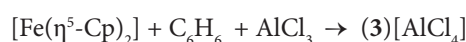

Fig. 5: Sterically strained arene complexes

Complexes with large fused arenes

Fused aromatic molecules, with a large delocalized π-electron cloud, form arene complexes by reducing the metal centre. For example, with Li or Na metal, naphthalene forms the reducing agents, metal naphthalide $[C_{10}H_8]^-$. $Li[C_{10}H_8]$ reduces $[CrCl_6]_4^-$ to form $[Cr(\eta^6-C_{10}H_8)_2]$ (**9**). The superbenzene (**10**) also forms arene metal complexes, *e.g.* sandwich complexes such as $[(\eta^5-Cp^*)Rh(\eta^6-\mathbf{10})]$, $[(\eta^5-Cp^*)Ru(\eta^6-\mathbf{10})]^+$ and $[(\eta^5-Cp)Fe(\eta^6-\mathbf{10})]^+$; and the half-sandwich complex $[(OC)_3Cr(\eta^6-\mathbf{10})]$, $(Cp^* = C_5Me_5)$.
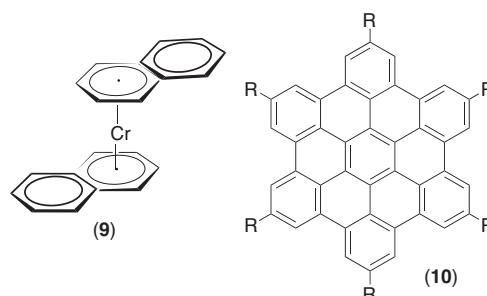
Other common synthetic routes to half-sandwich complexes are given below.

$[M(\eta^6-C_6H_6)_2] + [M(CO)_6] \rightarrow 2 \,(\mathbf{1})$

$[Fe(\eta^5-Cp)_2] + C_6H_6 + AlCl_3 \rightarrow (\mathbf{3})[AlCl_4]$

$RuCl_3 \cdot nH_2O \xrightarrow{} [(\eta^6-C_6H_6)RuCl(\mu-Cl)]_2$

Phellandrene can reduce $RuCl_3$ to form the dimer $[(\eta^6-Cymene)RuCl(\eta-Cl)]_2$. Reaction of $Ph_3Cr(THF)_3$ with $MeC≡CMe$ produces $[Ph_3Cr(\eta^6-C_6Me_6)]$.

Note: other small arenes such as cyclopropenyl (η^3-$C_3H_3^-$), cyclobutadiene (η^4-C_4H_4) and cyclopentadienyl (η^5-$C_5H_5^-$) ligands also form sandwich and half-sandwich complexes; their synthesis and reactions will not be discussed here.

Reactions of half-sandwich complexes

Upon coordination, the electron density of the π-cloud of the arene is reduced. Thus, when compared to benzene, the coordinated arene is less susceptible to electrophilic attack but more susceptible towards nucleophilic attack. Some of the reactions of $[(\eta^6-C_6H_6)Cr(CO)_3]$ (**1a**) are given below.

When (**1a**) is treated with BuLi, the lithiated arene complex (**11**) is formed. (**11**) serves as a nucleophile and reacts with I_2, CO_2/H^+ and Ph_2PCl to yield complexes
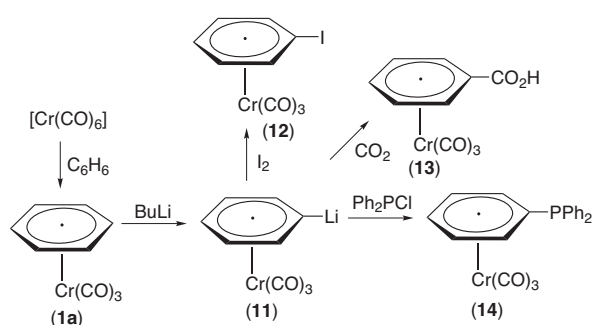
(**12**), (**13**) and (**14**), respectively.

Fig. 6: Synthesis & reactions of (**1a**)

The type and reactivity of the nucleophile, and the conditions used (*e.g.* reaction temperature) determine the final product of the reaction. Some of the reactions of $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$ (**15**) are given in Fig. 7.
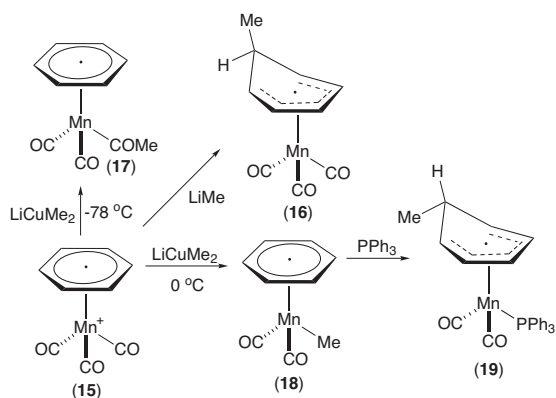

Fig. 7: Reactions of (**15**)

With MeLi, the cation (**15**) undergoes nucleophilic addition to form (**16**) due to the *exo*-attack of the arene ring by the methyl anion. At -78 °C, with LiCuMe$_2$, methyl anion attacks the carbonyl ligand to form acetyl-complex (**17**). At 0 °C, the methyl anion attacks the metal centre to form methyl-complex (**18**). In the presence of PPh$_3$, (**18**) affords the *endo*-product (**19**) *via* intramolecular methyl transfer to arene ring.

Arene complexes undergo nucleophilic substitution reactions, for example, the complex (**20**) with MeONa yields (**21**).
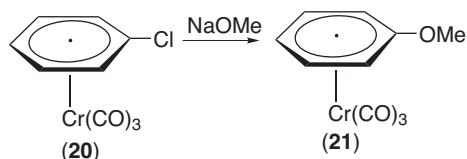

Fig. 8: A nucleophilic substitution reaction

Reactions of bis(arene) complexes

Homo sandwich or bis(arene) complexes (**2**) are air sensitive and get oxidized to form stable 17e cations. Mono- and dilithiation (or deprotonation) of (**2a**) can be achieved to form (**22**) and (**23**), respectively. Some reactions of (**22**) and (**23**) are summarized in Figs. 9 and 10 respectively. Reaction of (**22**) with acetyl chloride forms (**25**) resulting in ring expansion.
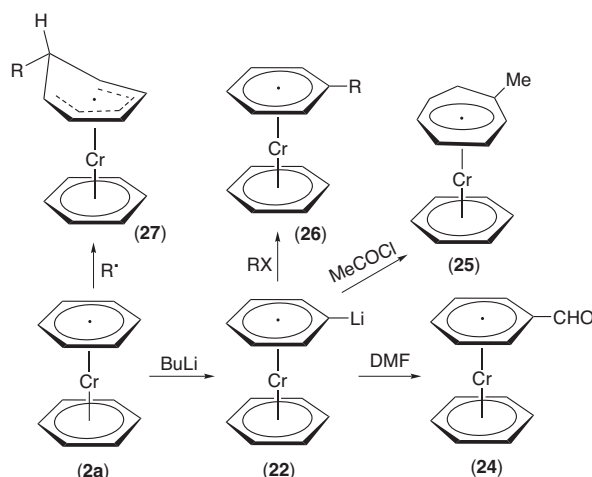

Fig. 9: Reactions of (**2a**) and (**22**)

The dilithiated product (**23**) can be used to introduce two functional groups on to both arene rings as shown in Fig. 10.
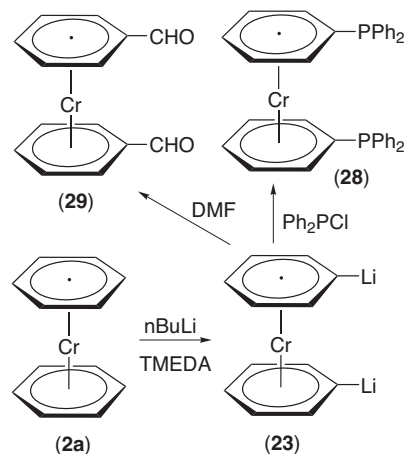

Fig. 10: Reactions of (**23**)

Ligand exchange reactions

It is observed that the metal prefers to bind to a ring with the highest aromaticity. Thus, the metal center exchanges bound arene(s) in the presence of arene ligand(s) with higher aromaticity. For example, Cr(0) exchanges naphthalene in (**9**), for phenanthrene forming (**30**) as shown below.
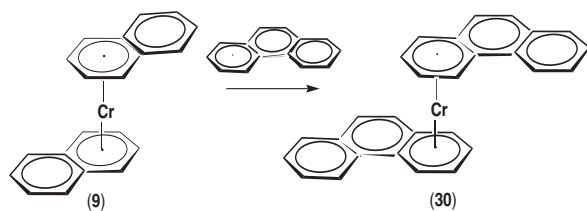
Fig. 11: A Ligand exchange reaction

Usually, the exchange of a free arene with the coordinated arene requires high temperatures. This ligand exchange can take place either (i) *via* a dissociative pathway, where the coordinated arene dissociates first followed by the coordination of the free arene or (ii) *via* an association, in which bonding of free arene and dissociation of bound arene takes place simultaneously.

Problems

1. Suggest possible product/s for the following reactions.

    (i)   (**1a**) + PPh$_3$ → (substitution)

    (ii)   (**1a**) + K → (reduction)

    (iii)   (**1a**) + NaOMe → (addition)

(iv)   (**15**) + 3 MeCN → (substitution)

(v)   (**15**) + NaOMe/Et$_2$O → (addition)

(vi)   (**15**) + NaOMe/MeOH → (addition)

(vii)   (**2b**) + 3 PMe$_3$ → (substitution)

(viii) (**3**) + MeLi → (addition)

(ix)   [CpFe(η^6-C$_6$H$_5$Cl)]$^+$ + NaOMe →

(x)   [CpMn(η^6-C$_6$H$_6$)] + MeCOCl →

(xi)   [CpRe(η^6-C$_6$H$_6$)] + NaPh →

(xii)   [Re(η^6-C$_6$H$_6$)$_2$]$^{2+}$ + 2 LiPh →

(xiii) (**2a**) + 2 C$_6$Me$_6$ → (substitution)

(xiv)   [(η^6-C$_6$H$_6$)Cr(η^6-C$_6$F$_6$)] + BuLi →

(xv)   [(η^6-C$_6$H$_6$)RuCl(μ-Cl)]$_2$ + 2 PPh$_3$ →

(xvi)   [(η^6-C$_6$Me$_6$)Ru(η^6-C$_6$H$_6$)]$^{2+}$ + 2 Na →

(xvii) Mn(g) + C$_5$H$_5$Me + PhMe →

(xviii) (**9**) + 3 PPh$_3$ → (substitution)

(xix)   (**9**) + 3 bipyridine → (substitution)

(xx)   (**2a**) + NaH → (addition)