

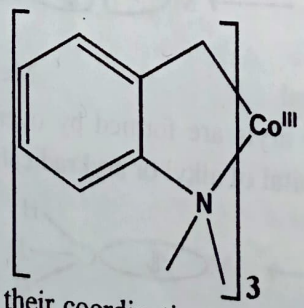
Transition Metal Aryl & Alkyl Complexes

hydrocarbon radical depends on the presence/absence of hydrogen atoms in that group. Presence of excess of hydrogen on the group makes it rather more positive, while absence of hydrogen or presence of electronegative F, Cl or O atom makes hydrocarbon radical more negative increasing the stability of M-C bond. Thus in summary, in comparison to alkyl or aryl compounds, fluoro alkyls or fluoro aryls have higher stability. Example: $\text{CF}_3\text{Co}(\text{CO})_5$ is far more stable than $\text{CH}_3\text{Co}(\text{CO})_5$. Fluorine makes M-C bond more polar by attracting electrons towards it increasing ionic contribution in that bond. Upon increase of positive charge on metal, d-orbitals get contracted which helps in increasing better overlap between bonding metal d-orbitals and ligand orbitals.

One important phenomenon takes place during synthesis of transition metal hydrocarbyls, which is the change of the nature of alkyl (or aryl) carbon from electrophilic to nucleophilic. Increase in $\text{M} \rightarrow \text{L}$ back-bonding (π -bonding) tendency is feasible with the increase in electroneutrality. This eventually increases stability of these compounds. Presence of CO, CN, pyridene etc. ligands (which help $\text{M} \rightarrow \text{L}$ π -bonding in transition metal alkyls or aryls) increases their stability, for example: $\text{Mn}(\text{CH}_2\text{CH}_3)(\text{CO})_5$, $\text{Mo}(\text{CH}_2\text{CH}_3)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ etc. are quite stable.

Most important characteristic of transition metal σ -hydrocarbyls is their coordinative unsaturation, leading to instability through facile decomposition paths. On the other hand, this unsaturation also explains their tendency to act as Lewis acids with a variety of donors. Presence of these ancillary ligands adds extra comparative stability on these derivatives. Examples: $\text{TiMe}_4(\text{bipy})$; $\text{TaMe}_5(\text{dme})$; $\text{CoMe}(\text{diphos})_2$, [diphos = 1,2-bis (diphenylphosphino) ethane], $\text{MMe}_2(\text{dmpe})_2$ [M=Ti, V, Cr, Mn and Fe, dmpe = 1,2-bis (dimethylphosphino) ethane], $\text{NiEt}_2(\text{bipy})$ and $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_n$ [Ln = lanthanide metal, $n = 2$ or 3] are more stable than uncoordinated σ -hydrocarbyls.

Chelating hydrocarbyls e.g. $o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2$ etc. tends to provide stability to σ -bonded derivatives by blocking the available coordination sites.

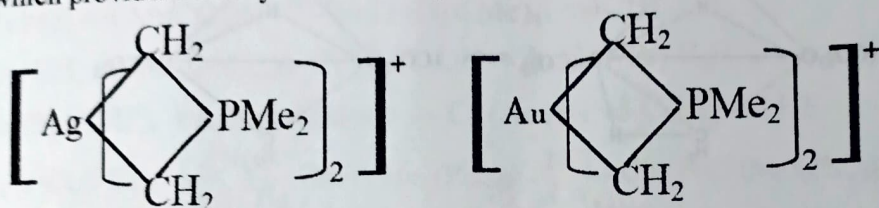


Metal-alkyl/aryls tend to satisfy their coordination environment by forming polynuclear species via alkyl or other bridging ligands or via multiple M-M bonding too. Association through bridging would obviously be hindered by sterically crowded ligands, resulting in mononuclear species. Though these complexes would formally be coordinatively unsaturated, still they will be thermally stable, due to steric crowding of the ligands which will inhibit any approach of reactive species. Example: $[\text{Ti}\{\text{CH}(\text{SiMe}_3)_2\}_3]$, $[\text{Cr}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ etc.

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Coordinative unsaturation increases upon lowering of the oxidation state of the metal, leading to greater associative tendency. For example, compared to the monomeric character of $Ti(C_6H_5)_4$, the polymeric nature of $\{Ti(C_6H_5)_2\}_n$ are cited more.

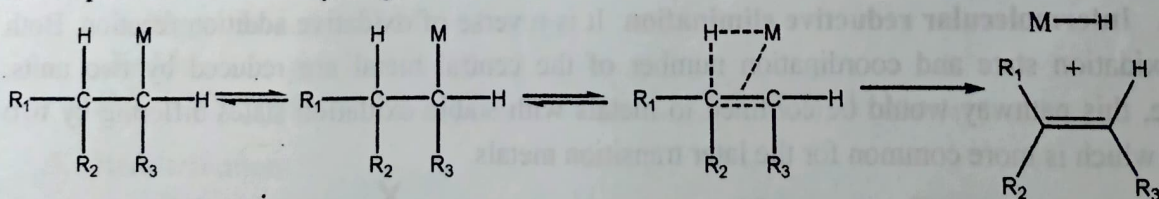
Transition metal σ -hydrocarbyls are of three types in nature: neutral, anionic and cationic. Stability of anionic species of the types $[Ti(C_6H_5)_5]^-$ and $[Zr(C_6H_5)_6]^{2-}$ can be explained as the central metal atoms are coordinatively less unsaturated than in their corresponding neutral species $[Ti(C_6H_5)_4]$ and $[Zr(C_6H_5)_4]$, respectively. With same logic, cationic species are expected to form not so easily. These often require a chelating hydrocarbyl of the type $Me_3P=CH_2$ for example, which provides stability on cationic species of the types:



Decomposition Pathways: Transition metals σ -hydrocarbyls, due to their coordinative unsaturation are not kinetically stable and this origins several facile pathways for their decomposition and strong reactivity. These paths can be classified as; (1) migration of a substituent (generally hydrogen) from a σ -bonded hydrocarbyl to the metal, (2) intermolecular reductive elimination and (3) homolytic fission of M-C bond.

1. **Migration of a substituent from a σ -bonded hydrocarbyl to the metal:** It occurs via 3 types of mechanism:

i. **β -elimination:** The most facile route for decomposition, preferred by transition metal alkyls is through the so called hydride transfer accompanied with alkene elimination. This type of reaction involves transfer of one hydrogen atom from the second or β -carbon atom of the alkyl chain to the metal, increasing its coordination number. Resulting intermediate hydrido-alkene complex tends to lose alkene upon formation of metal-hydride, which in some cases may decompose to metal and hydrogen too.



ii. **α -elimination:** α -Elimination pathways are much less observed for transition metal hydrocarbyls and main examples involve metal-methyls. However, these are of considerable synthetic utility in main group hydrocarbyls and involve the transfer of a substituent 'R' from the α -carbon atom to the metal. Binary permethyls, example: $TaMe_5$, WMe_6 and $ReMe_6$ are unstable and decompose explosively with the formation of methane via four-centred transition state. This plays a key role towards synthesis of alkylidene complexes. Several metal