Transition Metal - Alkyl and Aryl Complexes

CO2, SO2 or CS2 insertion: ii.

Cu Me(PPh₃)₃ $\xrightarrow{\text{CO}_2}$ Cu (O₂C Me)(PPh₃)₃ Cu Me (Et₂O) (PPh₃)₂ $\xrightarrow{CO_2}$ Cu(O₂C Me)(Et₂O)(PPh₃)₂ Au Me (PMe₃)₃ $\xrightarrow{SO_2}$ Au(SO₂ Me)(PMe₃)₃ Au Me₃ (PMe₃) $\xrightarrow{SO_2}$ Cis-Au Me₂ (SO₂Me) (PMe₃) Ti Me₂(η^{5} -C₅H₅)₂ $\xrightarrow{2SO_2}$ Ti (η^{1} -O₂ SMe)₂ (η^{5} -C₅H₅)₂

Organo-Copper in Organic Synthesis: Most important organocopper reagent is lithium dimethyl cuprate, Li[Cu(CH₃)₂], prepared by the action of methyl lithium with cuprous iodide:

 $4 \operatorname{LiCH_3} + \operatorname{Cu_2I_2} \rightarrow 2 \operatorname{Li}[\operatorname{Cu}(\operatorname{CH_3)_2}] + 2 \operatorname{LiI}$

paical characteristics of lithium dimethyl cuprate, Li[Cu(CH1)2] are

strong nucleophilicity towards carbon atom and very high affinity for reaction at alkene 1. Such stress compared to carbonyl groups. halide sites towards groups like cyano- or ester- etc.

In α, β — unsaturated carbonyl systems, it selectively attaches with β — Carbon atom. In, α, β —that special ability to replace various types of halogen atoms by methyl groups.

It has so that allylic acetates by SN² mechanism. geacts with epoxides to form open ring alkylated alcohols.

It adds to acetylene-esters.

haddition, there are examples of similar reactions involving branched alkyl, phenyl and vinyl apper reagents.

Halogen Substitution;

Trans-PhCH=CHBr + LiCuMe₂ -> Trans-PhCH= CHMe $C_6H_5I + LiCuMe_2 \rightarrow C_6H_5Me$

 $_{C_5H_{11}}Br + Li[Cu^tBu2] \rightarrow {}^tBu(CH_2)_4CH_3$

Oconjugated Additions:

1.4-addition of $\alpha.\beta$ -unsaturated carbonyl compounds

$$\begin{array}{c}
10 \\
+ R_2 Culi
\end{array}$$

the nucleophile is the pair of electrons in the Cu-CH₃ bond

AKP