Number: 5(dsp^3) Example: $TaMe_5$, Oxidation Number +5: Coordination Number: 6(d^2sp^3) Example: $[TaPh_6]^-$] are present in the group. General methods for synthesis are:

(i) **Halide exchange**:

$$VCl_2(dmpe)_2 + Li\ me \xrightarrow{ROR} Trans\text{–}V(Me)_2(dmpe)_2 + 2\ LiCl$$

$$VCl_3(THF)_3 + Li\ Ph \rightarrow VPh_3(THF)_3 + 3\ Li\ Cl$$

$$VCl_4 + 4\ Li\ R \rightarrow VR_4 + 4\ Li\ Cl\ (R = Me, Ph)$$

$$VCl_3(NMe_3)_2 + 3\ Li\ CH(SiMe_3)_2 \rightarrow V[CH(SiMe_3)_2]_3 + 3\ Li\ Cl + 2NMe_3$$

$$VCl_4 + 4\ Mg(CH_2Ph)\ x \xrightarrow[-60^\circ C]{ROR} V(CH_2Ph)_4 + 4MgXCl$$

$$VCl_4 + 4\ Li(CH_2SiMe_3) \longrightarrow V(CH_2SiMe_3)_4 + 4LiCl$$

$$Ta\ Cl_2\ Me_3 + 2\ Li\ Me \xrightarrow[+78^\circ c]{Et_2O} TaMe_5$$

(ii) **Transmetallation**:

$$Nb\ Cl_5 + ZnR_2 \xrightarrow{Pentane} NbCl_3R_2 + ZnCl_2$$

$$2TaCl_5 + 3ZnR_2 \xrightarrow{Pentane} 2TaCl_2R_3 + 3ZnCl_2$$

$$(R=Me,\ CH_2,\ Si\ Me_3)$$

4. **Group 6 - d^4 Metals:** Cr [Oxidation Number +2: Coordination Number: 4(dsp^2) Example: *Trans*-$CrMe_2(dmpe)_2$, 6(d^2sp^3) Example: $[Cr_2Me_8]^{4-}$; Oxidation Number +3: Coordination Number: 3(sp^2) Example: $Cr(CH_2Ph)_3$, 4(sp^3) Example: $[CrPh_4]^-$, 6(d^2sp^3) Example: $CrPh_3(THF)_3$; Oxidation Number +4: Coordination Number: 4(sp^3) Example: $CrMe_4$, 6(d^2sp^3) Example: $[CrMe_6]^{2-}$], Mo [Oxidation Number +2: Coordination Number: 5(dsp^3) Example: $Mo(CH_2Ph)(CO)_3(\eta^1\text{–}C_5H_5)$; Oxidation Number +3: Coordination Number: 6(d^2sp^3) Example: $(Mo_2Me_{10})^{4-}$; Oxidation Number +4: Coordination Number: 4(sp^3) Example: $Mo(CH_2Ph)_4$] and W [Oxidation Number +3: Coordination Number: 6(d^2sp^3) Example: $W_2Me_8^{2-}$; Oxidation Number +4: Coordination Number: 4(sp^3) Example: $W(CH_2Ph)_4$, 6(d^2sp^3) Example: WPh_6^{2-}; Oxidation Number +5: Coordination Number: 5(dsp^3) Example: $W(Ph)_5$; Oxidation Number +6: Coordination Number: 6(d^2sp^3) Example: WMe_6] are present in the group. General methods for synthesis are:

(i) Halide exchange method:

$$CrCl_2(dmpe)_2 + 2\ Li\ Me \xrightarrow{ROR} Trans\text{–}Cr\ Me_2(dmpe)_2 + 2\ Li\ Cl$$

$$CrCl_3 + 3\ Li\ CH(Si\ Me_3)_2 \longrightarrow Cr\{CH(Si\ Me_3)_2\}_3 + 3LiCl$$

$$CrCl_3 + 6\ Li\ Me \xrightarrow[-18^\circ c]{Dioxane} Li_3[Cr\ Me_6]_3 + 3LiCl$$

$$WCl_6 + 6AlMe_3 \rightarrow WMe_6 + 6\ AlClMe_2$$

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(ii) **Transmetallation:**

$CrCl_3(THF)_3 + AlR_3 \xrightarrow{THF} CrRCl_2(THF)_3 + AlR_2Cl_2$ (R = me, Et, Pr or ^tBu)

$WCl_6 + MR \rightarrow WCl_5R$ (MR = $HgMe_2$ (Ether), R = Me

= $ZnMe_3(CH_2Cl_2$ in Ether) R = Me

= $ZnPh_2$ (in Ether) R = Ph

= $SnMe_4$ (in Hexane) R = Me

(iii) **Reaction of Anionic Metal Complexes with Organic Halides:** Sodium salts of carbonilate are generally used in the synthesis of molybdenum hydrocarbyls. Example:

$Na[Mo(CO)_3\ \eta^5\text{-}C_5H_5) + PhCH_2Cl \rightarrow Mo(CH_2Ph)(CO)_3(\eta^5\text{-}C_5H_5) + NaCl$

(iv) **Ylide synthesis:**

$Cr(CO)_5(PPh_3) + Ph_3P{=}CH_2 \rightarrow Cr(CH_2PPh_3)(CO)_5 + PPh_3$

$CrCl_3(THF)_3 + 3Li(CH_2PMe_3) \xrightarrow[\text{Strong Base}]{} Cr\left[\begin{array}{c} CH_2 \\ \diagup\ \diagdown \\ PMe_2 \\ \diagdown\ \diagup \\ CH_2 \end{array}\right]_3 + 3LiCl$

5. **Group 7 - d^5 Metals:** Mn [Oxidation Number +1: Coordination Number: $6(d^2sp^3)$ Example: $Mn(CF_3)(CO)_5$; Oxidation Number +2: Coordination Number: $4(sp^3)$ Example: $MnMe_2(dmpe)_2$; Oxidation Number +3: Coordination Number: $4(sp^3)$ Example: $[Mn(CH_2CMe_2PPh_3)_3]_2$] and Re [Oxidation Number +3: Coordination Number: $4(sp^3)$ Example: $Re_2(\mu\text{-}SiMe_3)_2(CH_2SiMe_3)_4$, $6(d^2sp^3)$ Example: $Re_2Me_8^{2-}$; Oxidation Number +4: Coordination Number: $6(d^2sp^3)$ Example: $Re_3(CH_2SiMe_3)_{12}$; Oxidation Number +6: Coordination Number: $6(d^2sp^3)$ Example: $ReMe_6$] are present in the group.

General methods for synthesis are:

(i) **Halide exchange**:

$MnCl_2 + 4LiMe \xrightarrow[ROR]{} Li_2[MnMe_4] + 2LiCl$

$MnCl_2 + 2LiMe \xrightarrow{dmpe} Trans\text{–}MnMe_2(dmpe)_2 + 2LiCl$

$MnCl_2 + 4LiCH_2SiMe_3 \rightarrow Li_2[Mn(CH_2SiMe_3)_4] + 2LiCl$

$2MnCl_2 + 4MgCl[CH_2C(Ph)Me_2] \xrightarrow{ROR} [Mn\{CH_2C(Ph)Me_2\}_2]_2 + 4MgCl_2$

$3ReCl_4(THF)_4 + 6MgR_2 \rightarrow Re_3R_{12} + 6MgCl_2$

(ii) **Reactions of anionic metal complexes with organic halides**:

$Na[Mn(CO)_5] + CH_3I \rightarrow MnCH_3(CO)_5 + NaI$

$Na[Mn(CO)_5] + CF_3COCl \rightarrow Mn(COCF_3)(CO)_5 + NaCl$

(iii) **Insertion of unsaturated compounds in M-C bond**:

$MnPh(CO)_5 + PPh_3 \rightarrow Mn\{(CO)Ph\}(CO)_4(PPh_3)$

$MnCH_3(CO)_5 + CO \rightarrow Mn\{CO)CH_3\}(CO)_5$

A.K.R