C60J CHEMICAL SYNTHESIS

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1. **Introduction**
2. **Synthetic techniques**
3. **Role of solvents in synthesis**
4. **Surface Reactions (modifications) and catalysis at Surfaces**
5. **Zeolites**
6. **Electrical material-**
7. **Metal-Ligand Multiple Bond Chemistry**

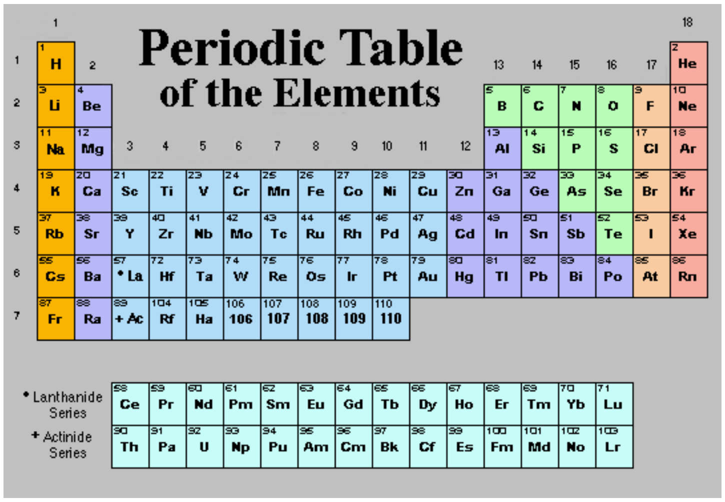
Why Synthesis

1. Curiosity ?

e.g. The discovery of the chemistry of Boranes

Alfred Stock-

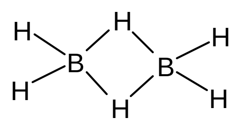
Boron Chemistry- due to the strong affinity of boron to oxygen Boric acid (H_3BO_3) dominates the chemistry of boron in oxygen atmosphere, *i.e.* nature.



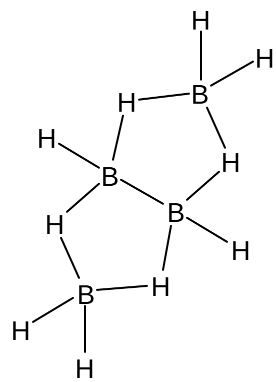
C vs. B

Hydrides of Boron-

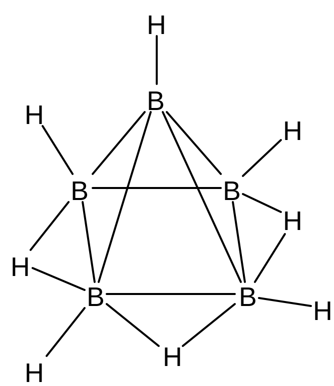
e.g. **B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, $B_{10}H_{14}$, $B_3N_3H_6$…..**



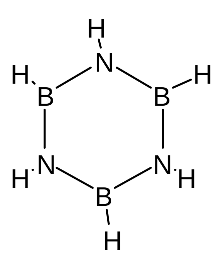
B_2H_6



B_4H_{10}



B_5H_9



$B_3N_3H_6$

-Chemistry of Boron hydrides are rich and has many uses in organic synthesis (hydroboration- H. C. Brown, Purdue University), fuels, medicine and many others.

Look for structures & reactivity-

Reference

1. B. Douglas, D. H. McDaniel and J. J. Alexander, Concepts & Models of Inorganic Chemistry, 2nd Edition, Wiley, 1982,

2. F. A. Cotton and J. Wilkinson, Advanced Inorganic Chemistry, 5th Edition, Wiley.

3. M. G. Davidson, A. K. Hughes, T. B. Marder and K. Eade, Contemporary Boron Chemistry, RSC publication.

(H. C. Brown-Purdue University-West Lafayette, Indiana, USA)

C vs. B

The chemistry of boron was limited to boric acid (H_3BO_3)
(H. C. Brown-Purdue University-West Lafayette, Indiana, USA)

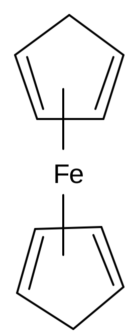
2. Accidental Discovery

Simple chance + careful observation ?   new compounds

Look for changes in color, precipitate formation, gas evolution, yield of unexpected product …..

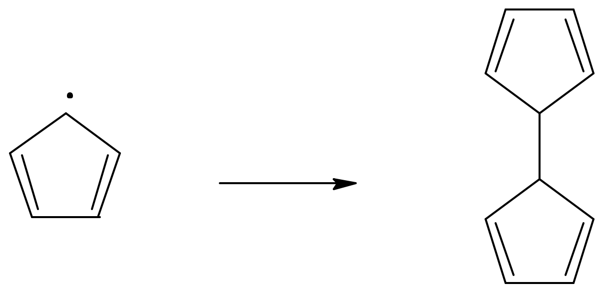
Try to find out what 'went wrong' ?   significant & spectacular discoveries.

E.g. **Synthesis of Ferrocene [$Fe(C_5H_5)_2$]**



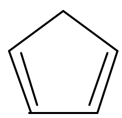
Kealy & Pauson:

Attempted to prepare dihydro fulvalene



dihydro-fulvalene

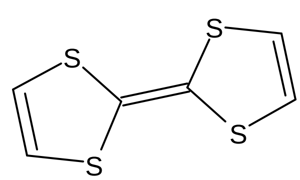
$FeCl_3$



+ $MgBr_2$? MgCpBr ($Cp = C_5H_5$)

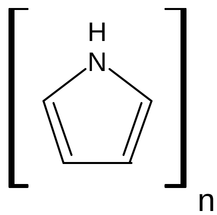
$2MgCpBr + FeCl_2$? $Fe(Cp)_2 + MgBr_2 + MgCl_2$

Tetrathiafulvalene

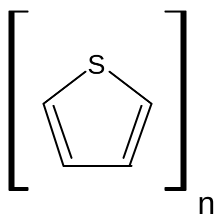


Problem Set #1

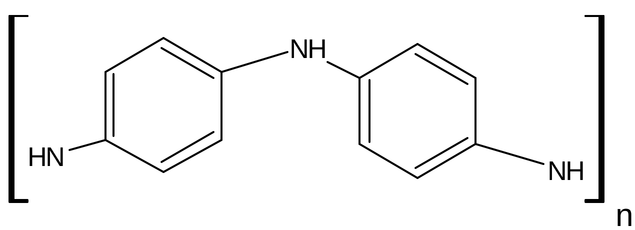
Polypyrol

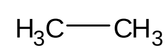


Polythiophine

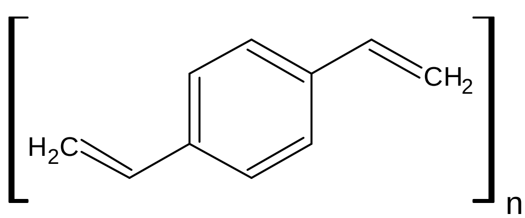


Polyanaline

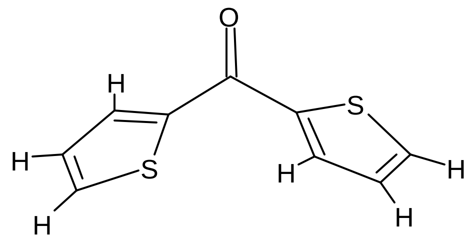




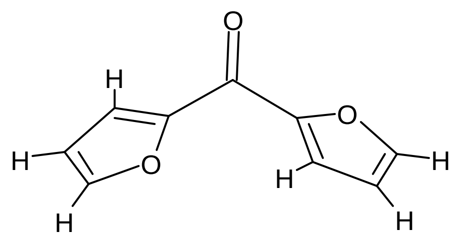
Polyphenylenevinylene



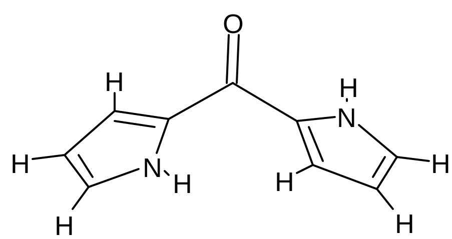
di-thienyl ketone



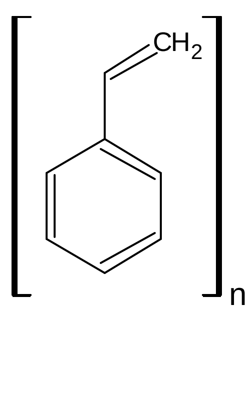
di-furyl ketone



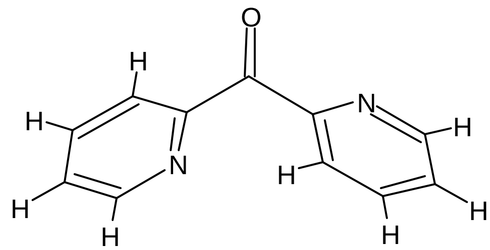
di-2-pyrolketone



poly-vinylpyridine



di-2-pyridyl ketone



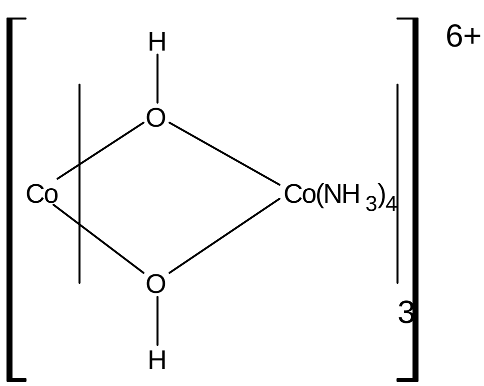
3. Test theories

Alfred Werner-1893-Optical isomerism of hexacoordinate compounds.

cis-$[Co(en)_2(NH_3)Br]^{2+}$ resolve into + & - form.

Optical activity thought to be centered on Carbon atoms of ethylenediamine (optically inactive), but Warner insist that optical activity is due to the geometrical configuration arount the metal center.

Isolated a compounds that does not have carbon.



4. Fulfill needs

New compounds because they are urgently needed:

e.g. preparation of CeS to handle molten U (uranium) & Pu (Plutonium) and avoid oxidation by oxygen.

Boron hydrides:

$U(BH_4)_3(BH_3CH_3)$ & $U(BH_3CH_3)_4$

To make volatile Uranium compounds.

5. Improve synthesis & New Methods for synthesis

What is needed?

1. Knowledge

i. Thermodynamics

$\Delta G = -RT\ln K = -nfE° = \Delta H - T\Delta S$
K = equilibrium constant, temp. variations

$\ln K = \Delta S°/R - \Delta H°/RT$

$d\ln K/dT = \Delta H°/RT^2$ **van't Hoff Equation**

ii. Descriptive Chemistry

Oxidants, reductants, acids, bases….

iii. Personal skills –

Solvents

Why solvents:

1. **Intimate contact between reactants. Homogeneous vs. heterogeneous reactions**
2. **Control reaction rate, *i.e.* reactions that are violent in the absence of a solvent may be carried out in a control fashion using solvent--- dilution effect**
3. **Control reaction conditions, e.g. temperature and polarity**
4. **Product separation utilizing solubility differences-polarity**
5. **Product analysis and characterization**
6. **Stabilize solid state structures-solvated crystals**

H_2O? common? cheap? purity? dissolve many compounds

Types:

a. Protic, e.g. H_2O and NH_3, HF and HCl

$$2NH_3 \longrightarrow NH_4^+ + NH_2^-$$

$$2HF \longrightarrow H^+ + HF_2^-$$

b. Aprotic-no hydrogen

e.g.

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

$$POCl_3 \longrightarrow POCl_2^+ + Cl^-$$

Solvations------ $POCl_3$----donor property of a solvent ----- tendency of a solvent to coordinate.

AQUEOUS VS. NON-AQUEOUS

Or Coordinating and Non-coordinating solvents

Solvent Purification

a. Distillation
b. Drying (drying agent)

Purify to avoid side reactions by impurities

------most frequent impurity in non-aqueous solvents

1. H_2O, removed by ketyl reagent
Na

$(C_6H_5)_2CO$ + Na ___________ $(C_6H_5)_2CO^{\cdot -}$ Na_{+}

Caution: Na ===== vigorously react with H_2O

2. **Peroxides:**

a. Water soluble peroxide

Test I$_2$(aq) in H^+ ? brown? confirm peroxide

Reflux in the presence of $Cu^I Cl$, then distillation

b. Water insoluble peroxide

Test: 1 mg $(Na/K)_2Cr_2O_7$ in 1 ml H_2O then H_2SO_4 & ether? blue? confirm peroxide

Use $Fe^{II}SO_4$ in H_2SO_4 to remove peroxide.

Drying reagents:

$LiAlH_4$=== react with protic species and removes them from solvents

CaH_2==calcium hydride===reflux

KOH===== for amines

Silica (SiO_2) D > 300º and activated alumina (Al_2O_3) D > 500º

Desiccants

$CaSO_4$ drierite

CaO

$CaCl_2$

Solvent Polarity

Petroleum ether
Cyclohexane
CCl_4
Benzene
CH_2Cl_2
$CHCl_3$
$(CH_3CH_2)_2O$
$CH_3CH_2CO_2C_2H_5$
Pyridine
Acetone
n-PrOH
EtOH
MeOH
H_2O
CH_3COOH

increase polarity

Polarity scale

Donor or acceptor properties

i.e. ability of solvent to coordinate to a solute

Empirical parameters

Table 3 Solvent dependence of the MLCT absorption maxima of *fac*-$[Re(CO)_3(dpk)Cl]$ **1**, *cis*-$[Re(CO)_2(PPh_3)(dpk)Cl]$ **3** and *cis*-$[Re(CO)_2(PPh_3)\{(C_5H_4N)_2C(O)(OH)\}]$ **4** at 298 K

	E_{MLCT}/kJ mol^{-1}			
Solvent	**1**	**3**	**4**	(π^*) [42,43]
Triethylamine	300.61	251.35	318.20	0.14
Diethyl ether	305.21	253.48	323.36	0.27
Tetrahydrofuran	311.57	255.65	325.12	0.58
Dimethylformamide	319.90	261.12	332.34	0.88
Dimethyl sulfoxide	321.62	262.37	334.20	1.0
Carbon tetrachloride	291.81	246.18	326.00	0.29
Chloroform	302.13	250.03	329.60	0.58
Chlorobenzene	305.21	253.48	330.51	0.71
Methylene chloride	308.36	254.56	333.27	0.83
Mesitylene	302.13	252.41	323.36	0.41
Toluene	302.13	252.41	323.36	0.54
Benzene	302.13	252.41	326.90	0.59
Anisole	308.36	254.45	328.69	0.73
Pyridine	311.57	256.75	330.51	0.87

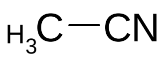
E_{MLCT} vs. Solvent parameters

References

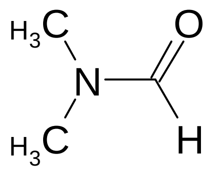
1. L. G. S. Brooker, A.C. Graig…. J. Am. Chem. Soc., 87, 2443, 1965.
2. C. Reichardt, Angew Chime Intern.Ed. Eng. 4, 29, 1965.
3. M. Bakir & J. McKenzie, J. Chem. Soc. Dalton Trans. 1997, 3571.

Solvent Reactivity

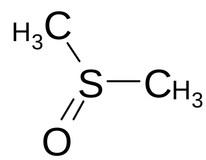
e.g. CH_3CN, DMSO, DMF, EtOH, CCl_4



Acetonitrile



dmf



dmso

NON-INNOCENT SOLVENTS

e.g.

$NbCl_3$ + dmso ——— $Nb(Cl_5)(dmso)$
oxygen bound

dmso

$NbOCl_3(dmso)_2$ + $(CH_3)_2SCl_2$

F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th Ed, Wiley, New York, 1988.

CCl_4 (oxidizing agent)

$$Re^{III}Cl_3(PR_3)_2 + CCl_4 \xrightarrow{\text{reflux}} Re^{IV}Cl_4(PR_3)_2$$

Free radical mechanism

Reactions of Alcohols

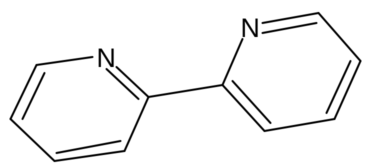
***trans-mer*-PhN=Re(PPh_3)$_2$$Cl_3$ + dppe**

EtOH | D

Ph_2PCH_2-CH_2PPh_2 (dppe)

***trans*- [PhN=Re(dppe)$_2$Cl]$^{2+}$**

***mer*-O=Re(bipy)Cl_3 + $PhNH_2$**



xylene | D

***mer*-PhN=Re(bipy)Cl_3 + H_2O**

EtOH
bipy | D

trans-[PhNRe(bipy)$_2$OEt]$^{+}$

1. **M. Bakir, S. Paulson, P. Goodson and B. P. Sullivan,** ***Inorg. Chem.*****, 1992, 31, 1129.**
2. Mohammed Bakir, and B. Patrick Sullivan, "Synthesis and Charachterization of phenylimidorhenium(V)compounds containing polypyridyl ligands. Crystal structures of ***mer*****-[Re(NPh)Cl$_3$(bipy)],** ***trans*****-[Re(NPh)(OEt)(bipy)$_2$]{PF$_6$]$_2$ and** ***trans*****-[Re(NPh)Cl$_2$(trpy)]PF$_6$ (bipy = 2,2'-bipyridine, terpy = 2,2':6',2"-terpyridine),"** ***J. Chem. Soc. -Dalton Trans.*** **, 1995, 1733.**
3. Mohammed Bakir, Jacinth A. M. McKenzie, and B. Patrick Sullivan, "The First Rhenium(V)-imido Compounds Containing Two Chelating Phosphine Ligands of the Type ***trans*****-[Re(NPh)X(L-L)$_2$]$^{2+}$ (L-L = bidentate phosphine ligand, X = halide or hydroxide). The Structure of trans-[Re(NPh)(OH)(dppbe)$_2$](ClO$_4$)$_2$.2H$_2$O,"** ***Inorg. Chim. Acta,*** **1997, 254, 9.**

$$[Ru_2Cl_3(PEt_2Ph)_6]Cl \xrightarrow{\text{EtOH, KOH}} RuHCl(CO)(PEt_2Ph)_3$$

$$RuCl_3.3H_2O \xrightarrow[\text{EtOH,reflux}]{PPh_3} RuHCl(CO)(PPh_3)_3$$

Advanced Inorganic Chem. 5th ed., F.A. Cotton & G. Wilkinson

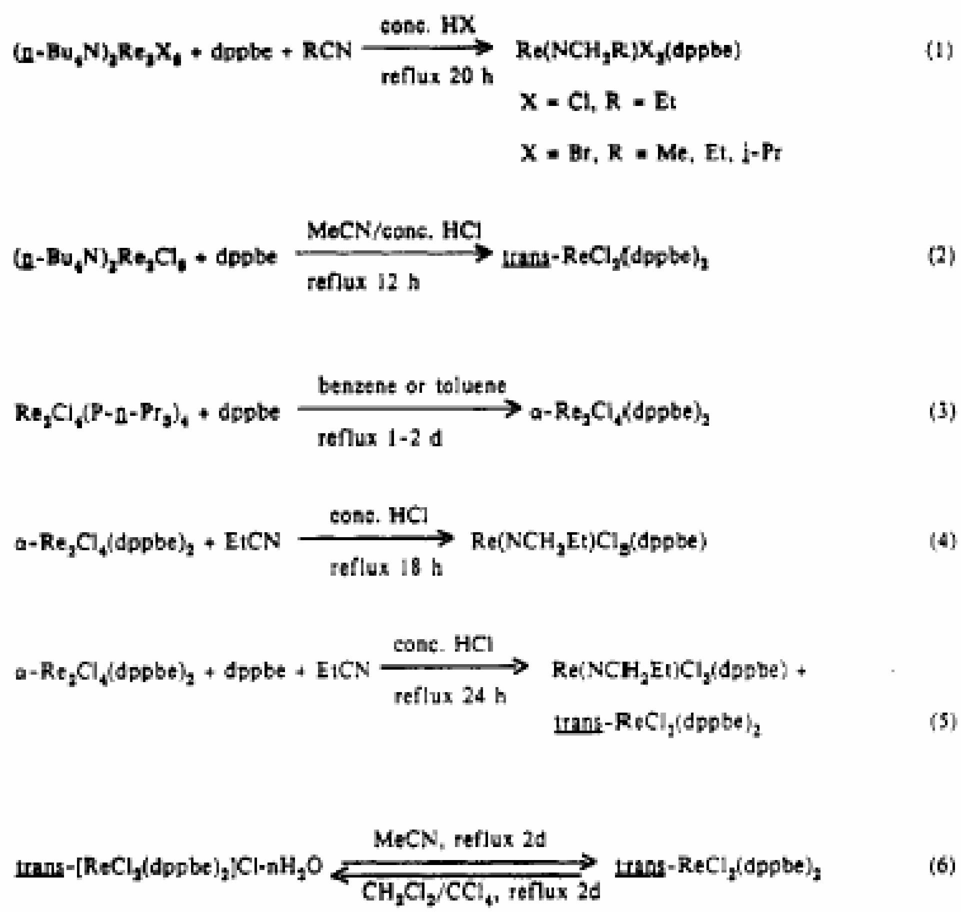
Nitriles

$$Re_2Cl_8^{2-} + L\text{-}L \xrightarrow{CH_3CN} Re(=NCH_2CH_3)Cl_3(L\text{-}L)$$

$$CH_3CN \longrightarrow CH_3\,CH_2N$$

$$Re = CH_2CH_3$$

Scheme I



1. M. Bakir, P. E. Fanwick & R. A. Walton, *Inorg. Chem.,* 1988, 27, 4197.

2. D. Esjorson, M. Bakir, P. E. Fanwick, K. S. Jones & R. A. Walton, *Inorg. Chem.*, 1990, 29, 2055.

Aqueous vs. Non-aqueous

trans-$[Os^{VI}{=}N(tpy)Cl_2]^+$

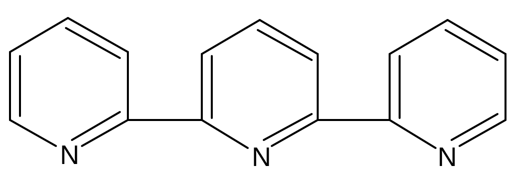
$+4e^-$ $3H^+$ $+e^-$ CH_3CN

$Os(NH_3)(tpy)Cl_2$

$[Cl_2(tpy)Os{-}N{=}N{-}Os(tpy)Cl_2]^{n+}$

CH_3CN

$[Cl_2(tpy)Os(NCCH_3)]^{0/1+}$



tpy

1. **Mohammed Bakir, David W. Pipes, S. Erasmus Vitols, Derek J. Hodgson, and Thomas J. Meyer, "The Reversible Interconversion Between Os(VI) Nitride to Os(II) Ammine," *J. Am. Chem. Soc.*, 1990, 112, 5507.**
2. **Mohammed Bakir, Peter S. White and Thomas J. Meyer, "Preparation of Os(IV)-phosphoraniminato Complexes Containing Polypyridyl Ligands.**

Nitrogen Atom Transfer from [Os^{VI}(tpy)$(Cl)_2$(N)]$^{+}$," *Inorg. Chem*., 1991, 30, 2835.

3. Konstantinos D. Demadis, Mohammed Bakir, Bert Klesczewski, Darryl S. Williams, Peter S. White, and Thomas J. Meyer, "Nitrogen Atom Transfer and Redox Chemistry of Terpyridyl Phosohoraniminato Complexes of Osmium(IV)", I*norg. Chim. Acta,* 1998, 270, 511.

Nitriles

$TiCl_3$ + RCN ———— $TiCl_3(NCR)_3$ blue

$Ti^{III}Cl_3$ + CH_2ClCN* ———— $TiCl_3(NCR)_3$

blue

|

$Ti^{IV}Cl_4(NCR)_2$

yellow

$TiCl_3$ + CCl_3CN ———— [$TiCl_4(CNCCl_3)$]

Free radical mechanism

$.CH_2CN$

[CH2CN]n

$CNCH_2CH_2CN$

$RuCl_2(PPh_3)_3$ —RCN→ $RuCl_2(RCN)_2(PPh_3)_2$

$TiCl_3 + Zr^{II}Cl_2 \xrightarrow{THF} trans-[TiCl_2(THF)_4]^+$

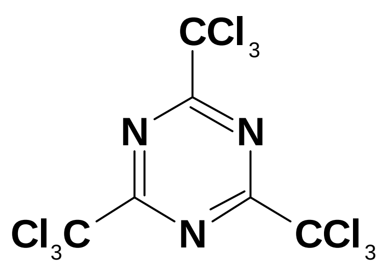
$+ Zr^{III}Cl_3(THF)$

$TiCl_3.3H_2O$ $ZrCl_2.2THF$

$TiCl_4 + RCN \longrightarrow TiCl_4(RCN)_2$

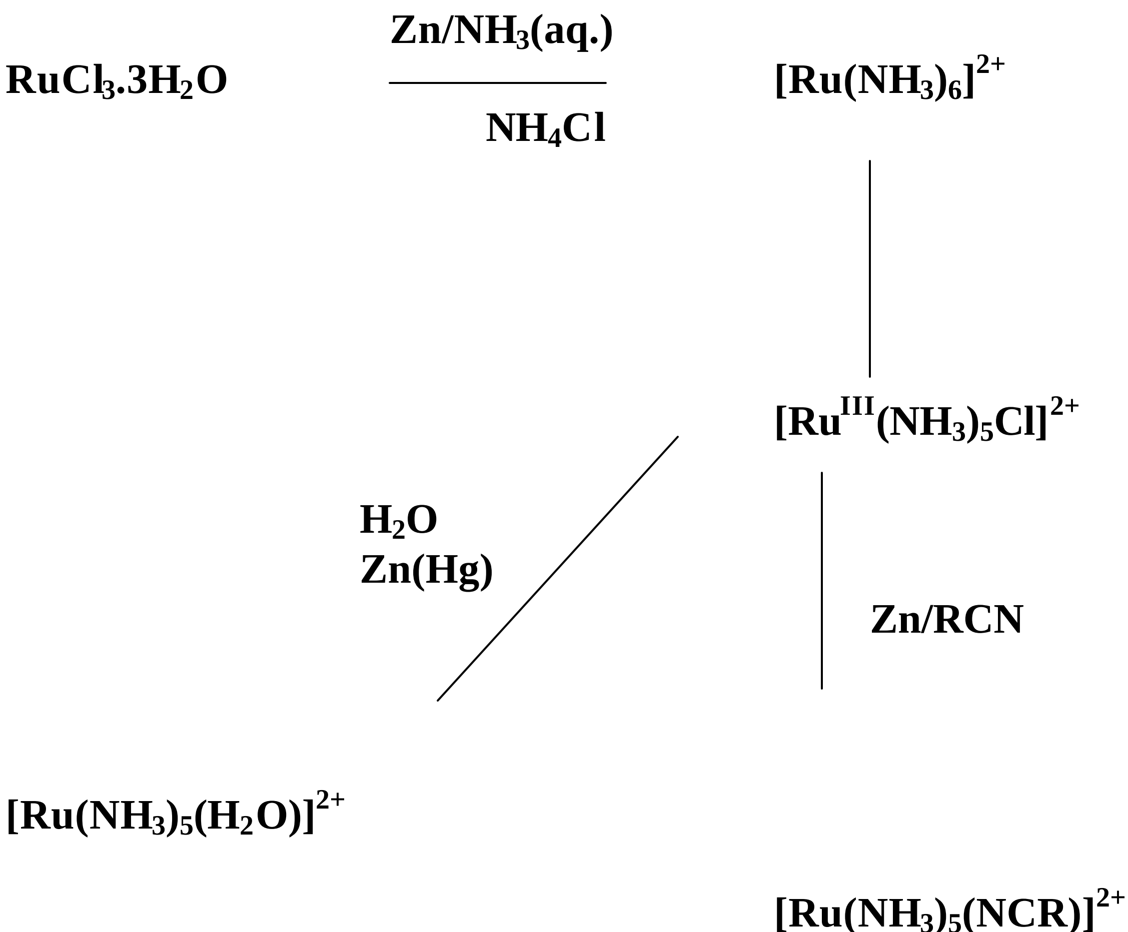
$VCl_4 + RCN \longrightarrow VCl_3(RCN)_3$

Organic byproduct



2-methyl-4,6-bis(trichloromethyl)1,3,5-triazine

$VO(acac)_2 + SOCl_2 \xrightarrow{\text{benzene, RT}} VCl_2(acac)_2 + SO_2$



Advanced Inorganic Chem. 5th ed., F.A. Cotton & G. Wilkinson