Metal-Ligand Multiple Bonds

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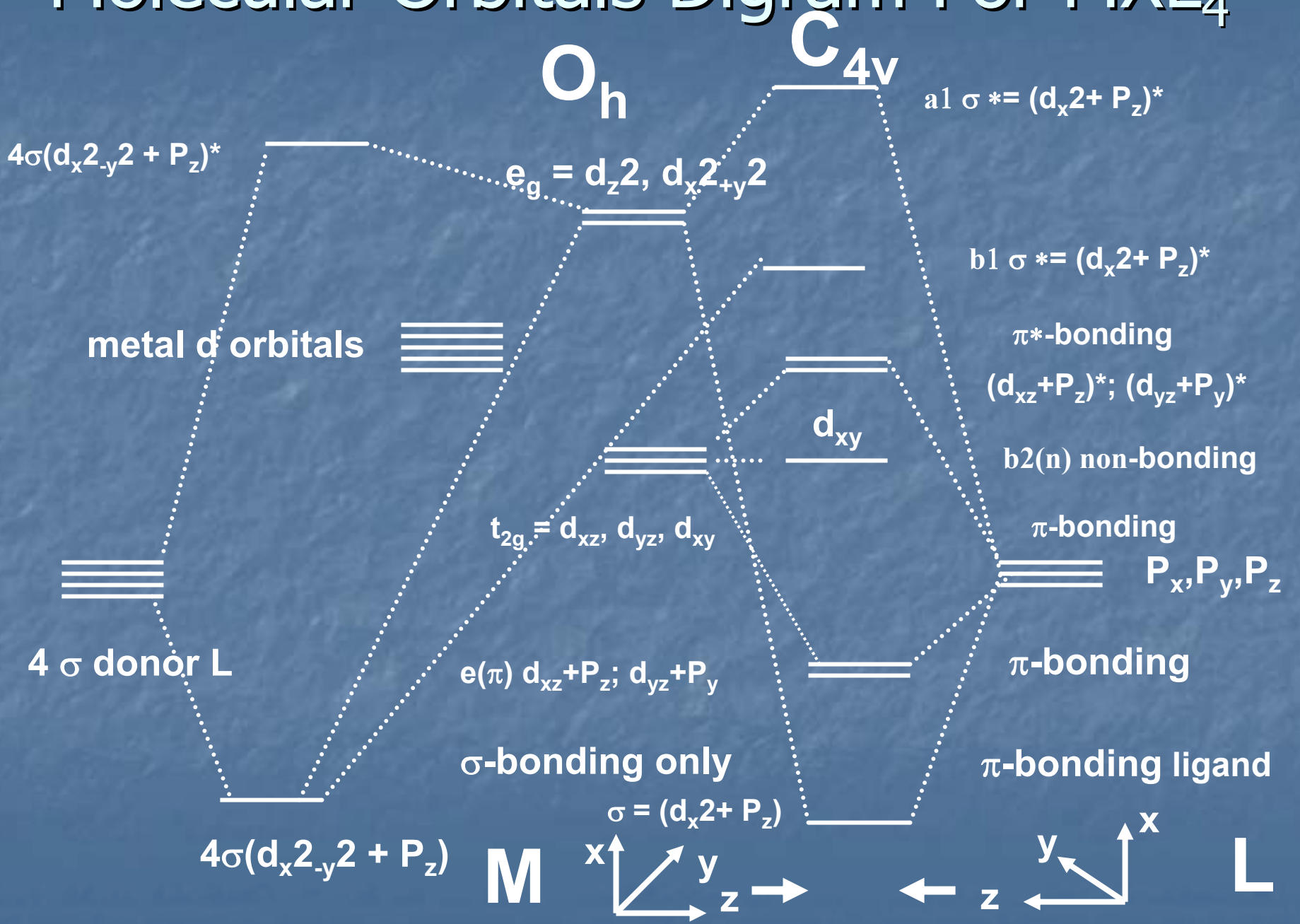
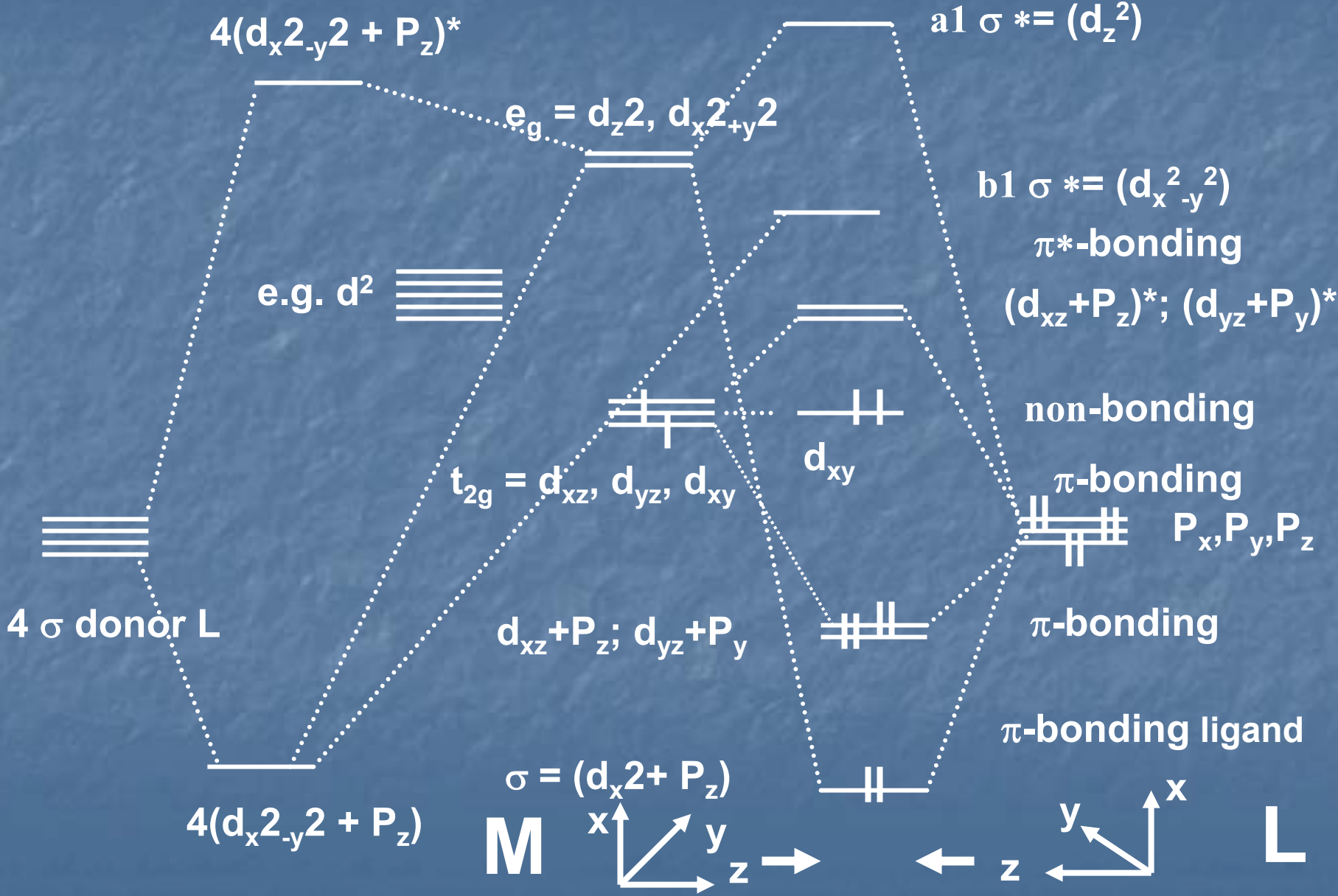
C60 J

Molecular Orbitals Digram For MXL_4



Electrons Count



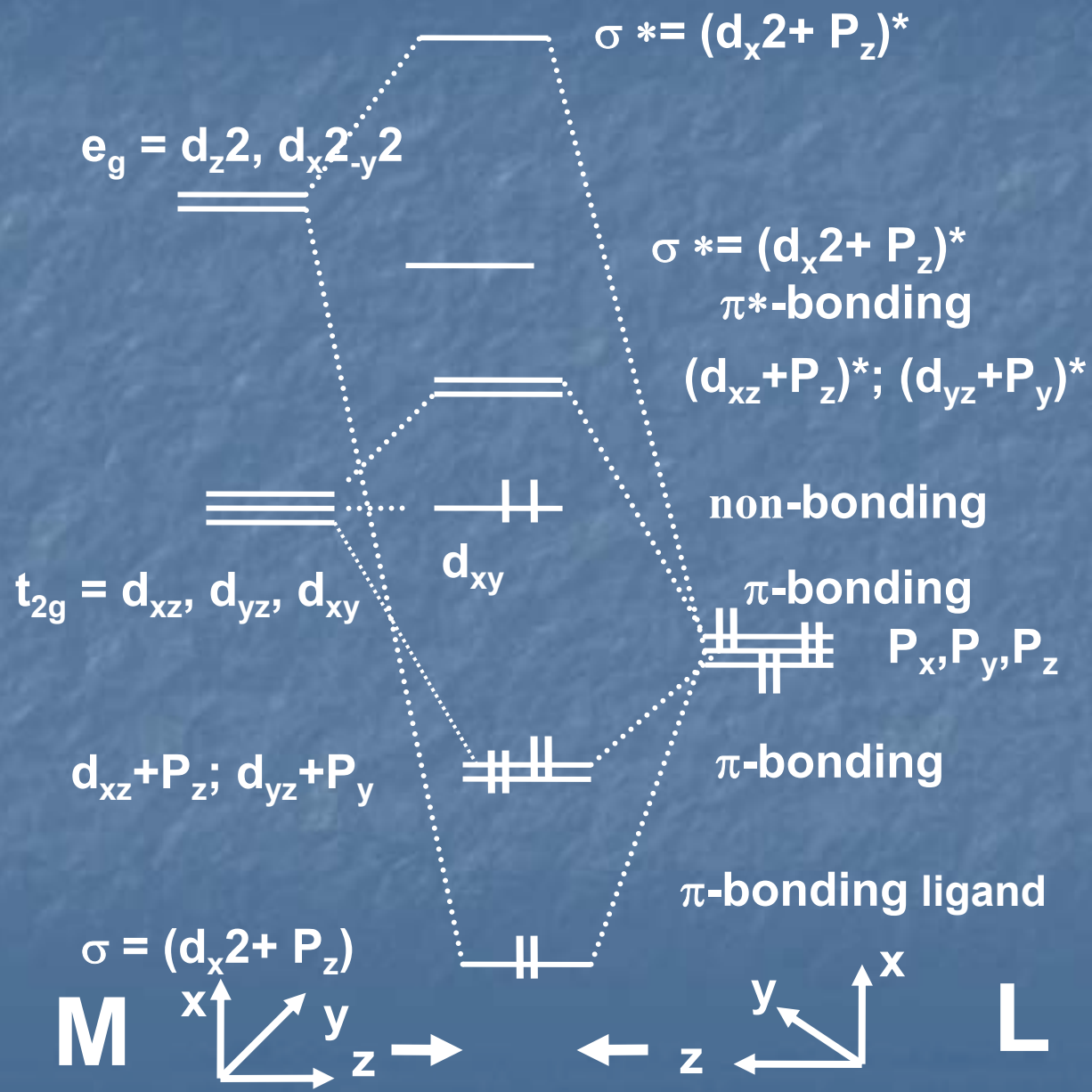
Bond Order

B.O = ½ (# B.E. -#A.E)
In case n = 0, 1, or 2,
Where n =m # d e's

B.O = 3 Stable

If > 2

Bond order less than 3
Not stable



Synthesis of T.M Compounds with Metal-Ligand Multiple Bonds

- Reference: A. A. Cotton & G. Wilkinson; Advanced Inorganic Chemistry, 5th Edition, Wiley
- Metal-Oxides
- Oxidation of metals
  - $M + O_2 \rightarrow MO_n$ (heat)
  - $MX_n + O_2 \rightarrow MO_nX_y$
  - $UCl_4 + O_2 \rightarrow UO_2Cl_2$ at 300 °C
- Reduction of MOn
  - $MO_4 + HX \rightarrow MO_xX_y$
  - $KReO_4 + HX \rightarrow [ReOX_y]^{-n}$ where y = 4 or 5 and n = 1 or 2
  - $KReO_4 + PPh_3 + HX \rightarrow ReOX_3(PPh_3)_2$

Synthesis of T.M Compounds with Metal-Ligand Multiple Bonds

- Metal Imides

- From Primary Amines
- $L_nMX_2 + H_2NR \rightarrow L_nMNR + 2HX$

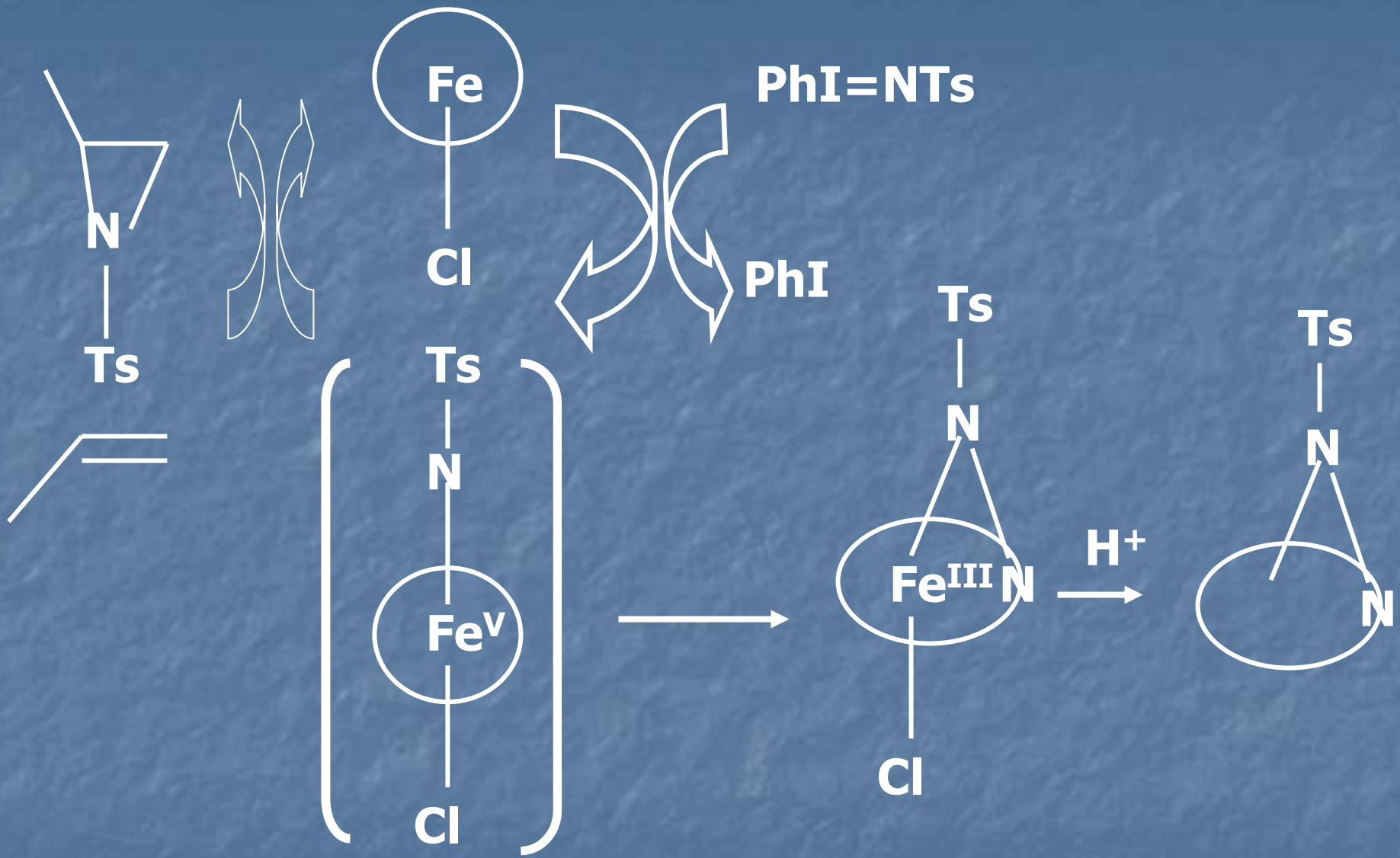
  - $WCl_6 + 10\ ButNH_2 \rightarrow (ButN)_2W(NHBut)_2 + 6\ Bu^tNH_3Cl$

- Metal dialkyamides
  - $Ta(NMe_2)_5 + RNH_2 \rightarrow (Me_2N)_3TaNR + 2Me_2NH$

- From Metal oxides
  - $L_nMO + H_2NR \rightarrow L_nMNR + H_2O$
  - $OsO_4 + RNH_2 \rightarrow O_3OsNR + H_2O$

Synthesis of T.M Compounds with Metal-Ligand Multiple Bonds

- From Silylamines
  - $L_nMO + RN(SiMe_3)_2 \rightarrow (Me_3Si)_2O + L_nMNR$
- From phosphinimine, isocyanates and sulfinylamines
  - $O_3OsNR + 2Ph_3PNR \rightarrow OOs(NR)_3 + 2Ph_3PO$
  - $L_2Cl_3ReO + Ph_3PNR \rightarrow L_2Cl_3ReNR + Ph_3PO$
  - $L_2Cl_3ReO + ArNXO \rightarrow L_2Cl_3ReNr + XO_2$ (X = S or C)



J. P. Mahy, P. Battioni, D. Mansuy, JACS, 1986, 108, 1079.

Synthesis of T.M Compounds with Metal-Ligand Multiple Bonds

- Metal Nitrides

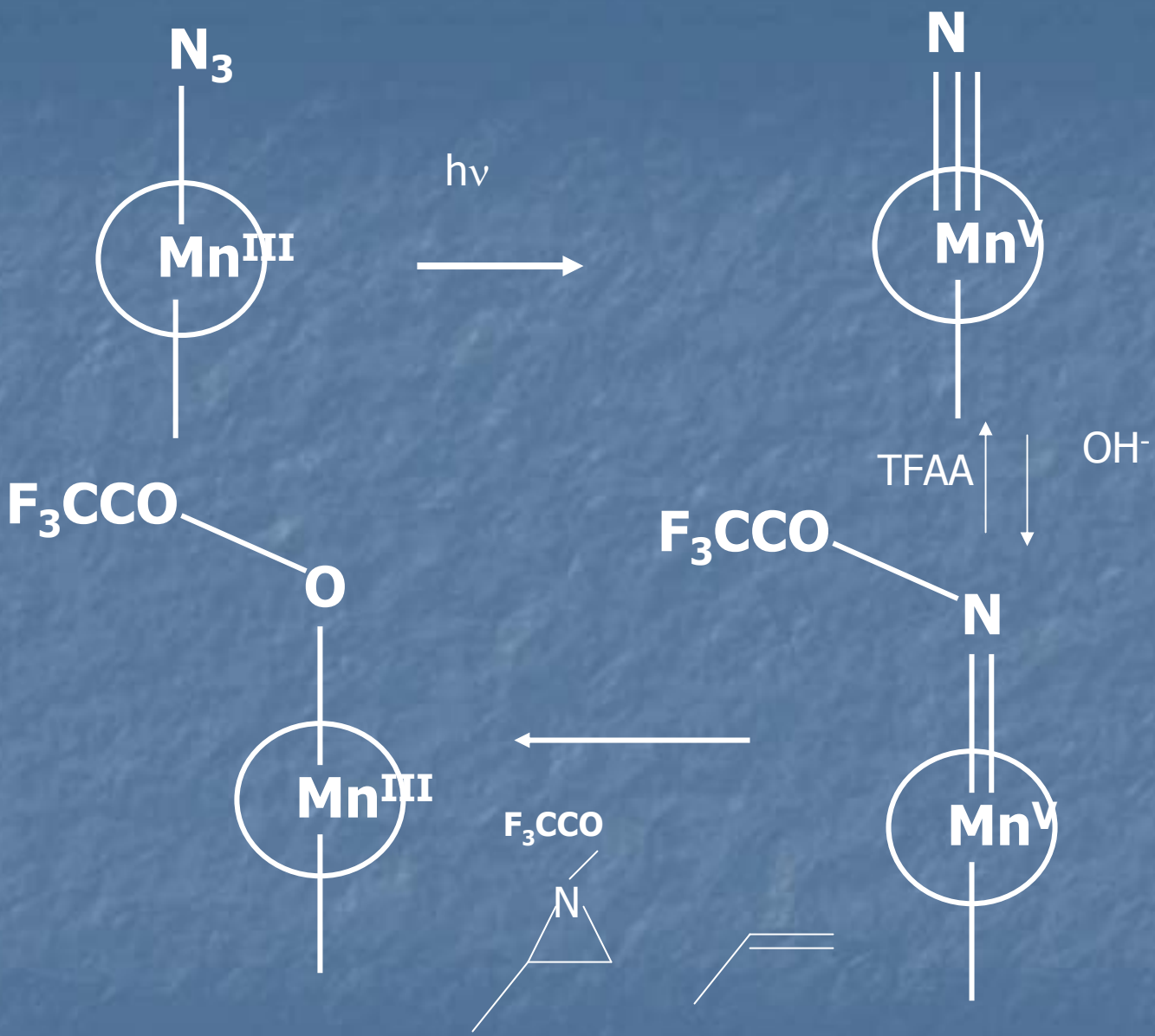
- From Primary Ammonia
- $Os^{VIII}O_4 + NH_4OH + KOH + HX \rightarrow [X_yOs^{VI}N]^{n-}$ (X = halide, y = 4 or 5 & n = 1 or 2)

- Nitride transfer
- $MnN(salen) + Cr(THF)_3Cl_3 \rightarrow [NMe_4]_2[Cr(N)Cl_4].H_2O$

  - JACS, 2003, 125(44): 13348-13349
  - Herdtwick and Herman (2002), J. Organometall. Chem. 660, 121-126.

Synthesis of T.M Compounds with Metal-Ligand Multiple Bonds

- Nitrogen splitting
  - L_xM^n-N2-M^nL_x –e's → M^YNL_n (n = 1, 2 and y = 4 or 5)
    - $[Ru(NH_3)_5H_2O]^{2+} + N_2 \leftrightarrow [(NH_3)_5Ru\text{-}N_2]^{2+}$
    - $[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+} \leftrightarrow [(NH_3)_5Ru\text{-}N2\text{-}Ru(NH_3)_5]^{4+}$
- From hydrazine
  - $KReO_4 + N_2H_4 + HX \rightarrow [ReNX_y]^{n-}$ (Y = 4 or 5 & n = 1 or 2)



J. T. Groves , T. Takahashi, JACS, 1983, 105, 2073