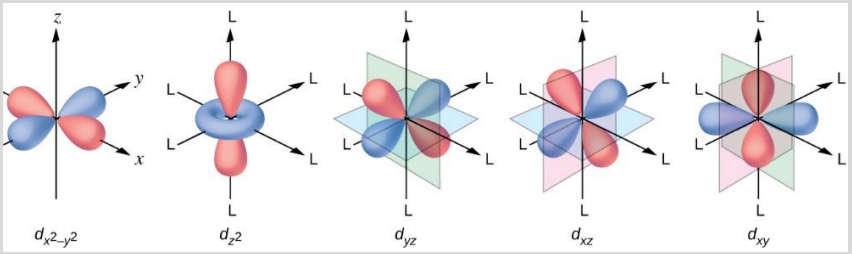
Ligand Field Theory 1: Covalent Bond Classification, MO Diagrams

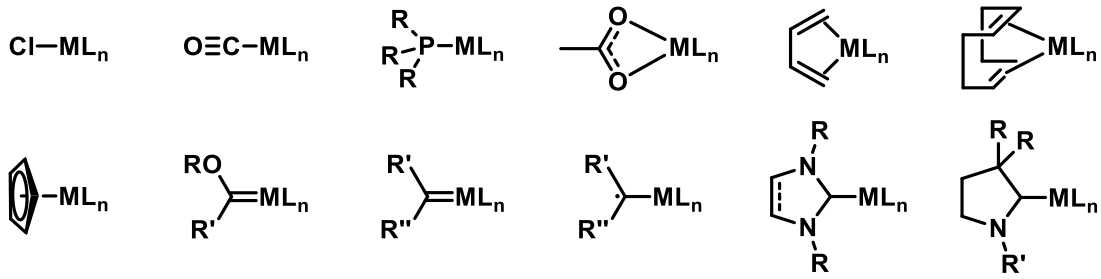
Models/Topics Covered: Ligand Field Theory, MO Theory, LXZ Notation, 18VE Rule, Covalent Bond Classification, Dewar-Chatt-Duncansen Model, Tolman Electronic and Steric Parameters



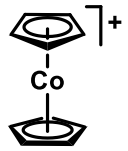
Reproduced from Ref[2] (Fig. 8.3.1)

Question 1 (Covalent Bond Classification)

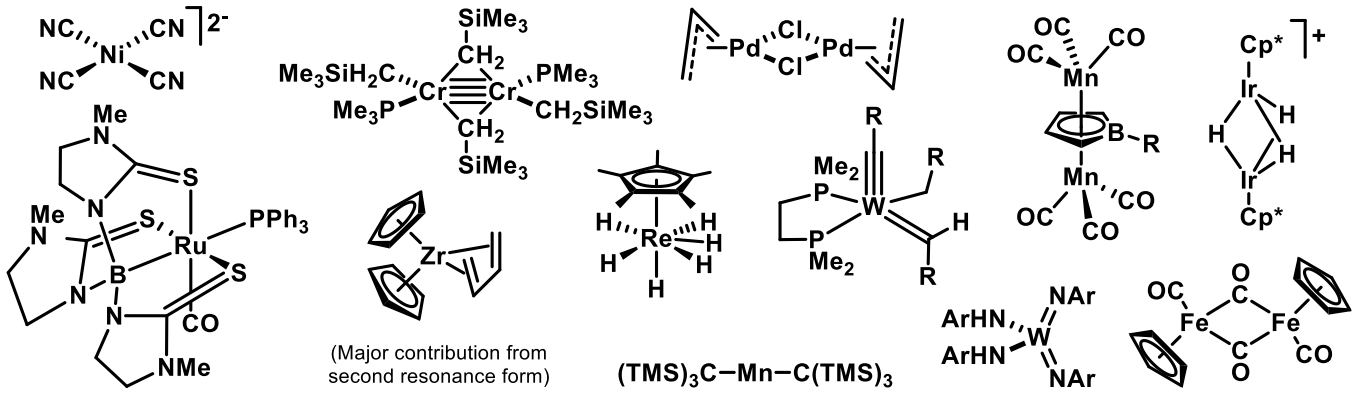
(i). For each diagram, give the name of the ligand class and indicate the donation type, in terms of LXZ notation.



(ii). Cobaltocenium ($CoCp_2^+$) is an 18VE species. Rationalise this using both ionic and covalent models of electron counting.

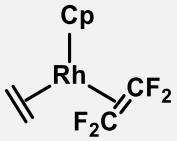


(iii). Provide full electron counts and metal oxidation states for the following species.



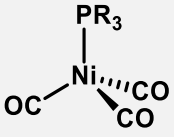
Question 2 (Selected Electronic and Steric Factors in Organometallic Complexes)

Two simple organometallic complexes are shown below. For the alkene, carbonyl, and phosphine ligands provide a diagram of orbital overlap and use this to rationalise the trend in the characterisation data given in each case.



SXRD Bond lengths:

- $H_2C{=}CH_2$: 1.35 Å
- $F_2C{=}CF_2$: 1.40 Å



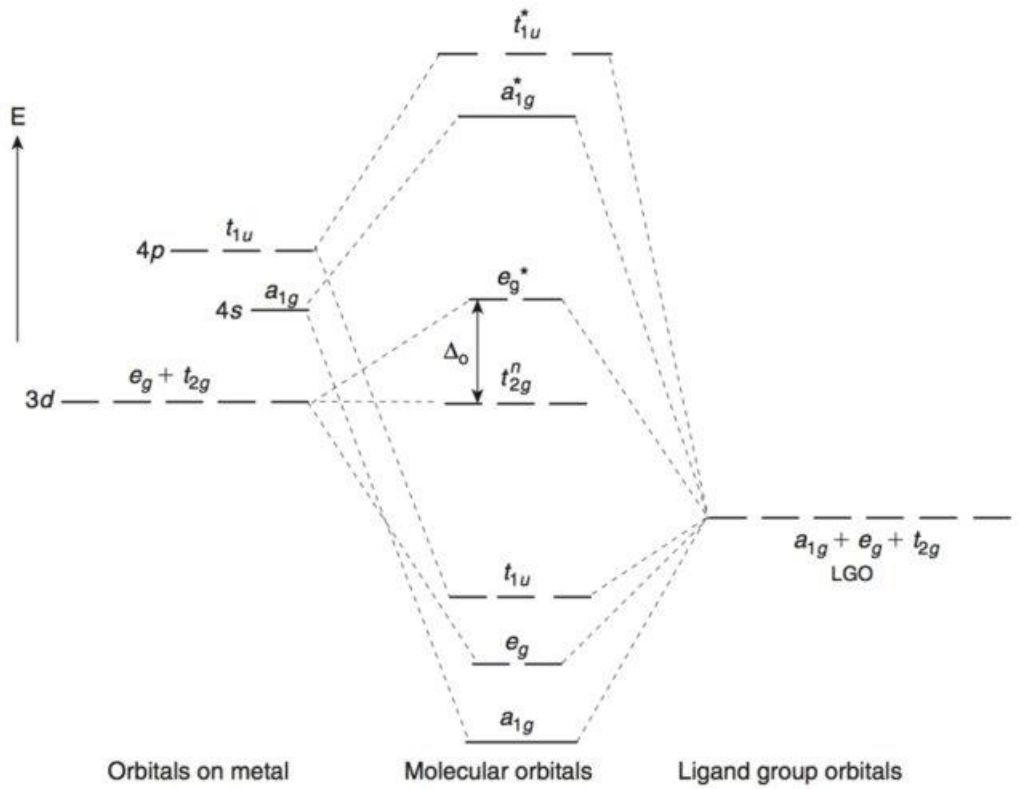
R_3	ν_{CO} / cm^{-1}	R_3	ν_{CO} / cm^{-1}
$^tBu_3$	2056.1	$MePh_2$	2067.0
Cy_3	2056.4	Ph_3	2068.9
$^iPr_3$	2059.2	$(OMe)_3$	2079.5
Et_3	2061.7	$(OPh)_3$	2085.0
Me_3	2064.1	Cl_2Ph	2092.1
Me_2Ph	2065.3	Cl_3	2097.0
$(o\text{-}C_6H_4Me)_3$	2066.6	F_3	2110.8

Question 3 (Spectrochemical Series)

The spectrochemical series for ligands is used to rationalise the size of Δ in Crystal Field Theory. However, the rationale for which ligands are strong or weak field is not explained well by this model. Ligand Field Theory offers a better explanation through consideration of the exact bonding between metal and ligand.

Using the MO Diagram for an octahedral ML_6 complex (below), indicate:

(i). the origin of the 18VE rule
(ii). why the following complexes are all 'stable', despite varied electron counts: $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Ni(H_2O)_6]^{2+}$
(iii). why salts of $[NbMe_6]^-$ are isolable (although β-hydride elimination occurs very quickly with longer alkyls)
(iv). why neither $Fe(CO)_6$ or $Ti(CO)_6$ complexes are common-place, and what form mononuclear carbonyl complexes of these two metals (in their neutral oxidation state) may take instead. Based on this reasoning, why does vanadium typically coordinate six carbonyls to form a mononuclear complex?
(v). the trend in Δ_O as shown by the spectrochemical series of ligands



Spectrochemical Series (Ligands):

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < N_3^- < F^- < ONO^- < OH^- < SO_4^{2-} < NO_4^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 \sim py < en < bpy \sim phen < NO_2^- < PR_3 < CH_3 < CN^- \sim CO$

Spectrochemical Series (Metals):

$Mn(II) < Ni(II) < Co(II) < Fe(II) < V(II) < Fe(III) < Co(III) < Mn(III) < Mo(III) < Rh(III) < Ru(III) < Pd(IV) < Ir(III) < Pt(III)$

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