MLXZ Classification for Organometallics

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Outline

Visit the Web Page of Ged Parkin

- Professor Ged Parkin of Columbia University Click here to visit Ged's web page
- Key concept number 1: CBC or Covalent Bond Classification method
- Practice finding the $[ML_lX_xZ_z]$ classification for a metal complex
- Some important definitions

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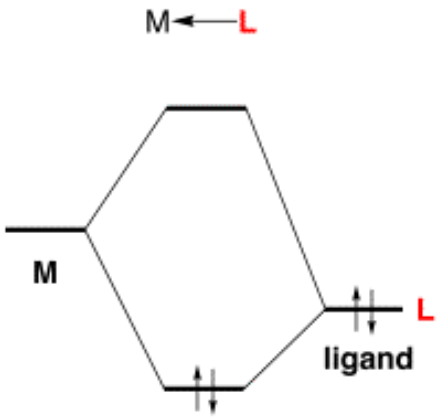
Three Basic Types of Interaction

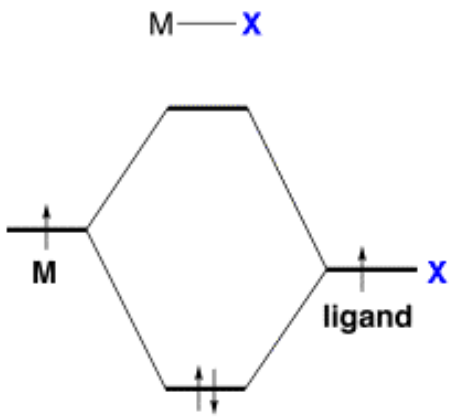
2-, 1-, and 0-electron neutral ligands



L ligand

both electrons provided by ligand
e.g. PR_3, CO, C_2H_4
(neutral molecules)

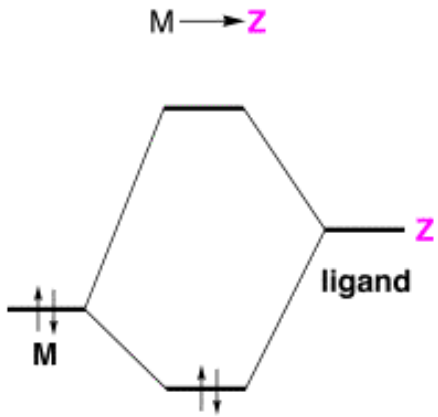
Dative Covalent Bond



X ligand

one electron provided by ligand and by metal
e.g. H, Cl, R
(radicals)

Normal Covalent Bond



Z ligand

both electrons provided by metal
e.g. BF_3
(Lewis acids)

Dative Covalent Bond

An **L**–function orbital is occupied by a **pair** of electrons.

An **X**–function orbital is filled by a **single** electron.

A **Z**–function orbital is **empty**.

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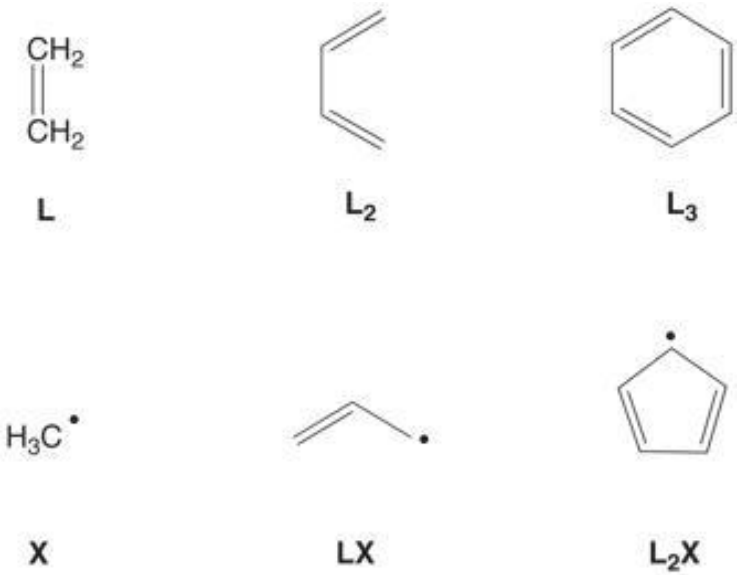
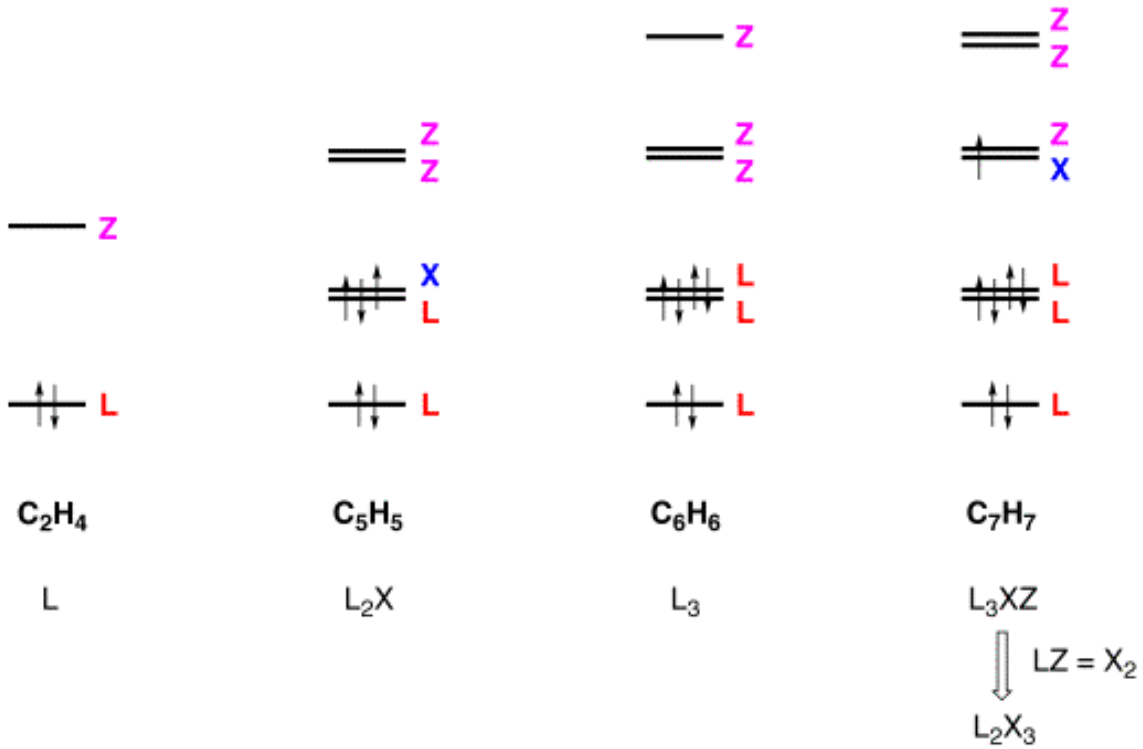
Some Examples of Ligand Classification

Some standard organometallic ligands



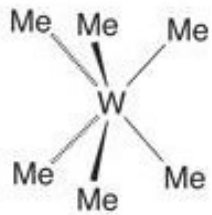
Further Examples of Ligand Classification

Some standard organometallic ligands



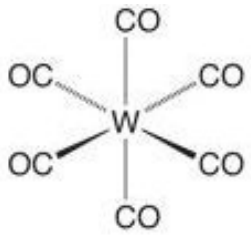
Classifying Some Organometallic Molecules

Looking at the species as a whole



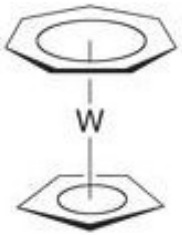
6 Me X_6

MX_6



6 CO L_6

ML_6



1 (C_5H_5) L_2X

1 (C_7H_7) L_2X_3

ML_4X_4

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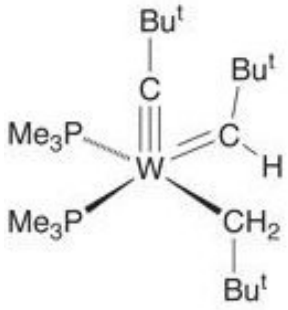
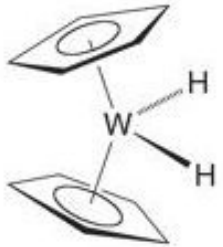
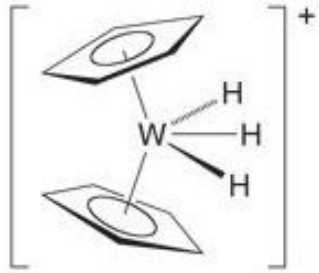


2 PMe_3	L_2
1 CH_2Bu^t	X
1 $CHBu^t$	X_2
1 CBu^t	X_3
ML_2X_6	



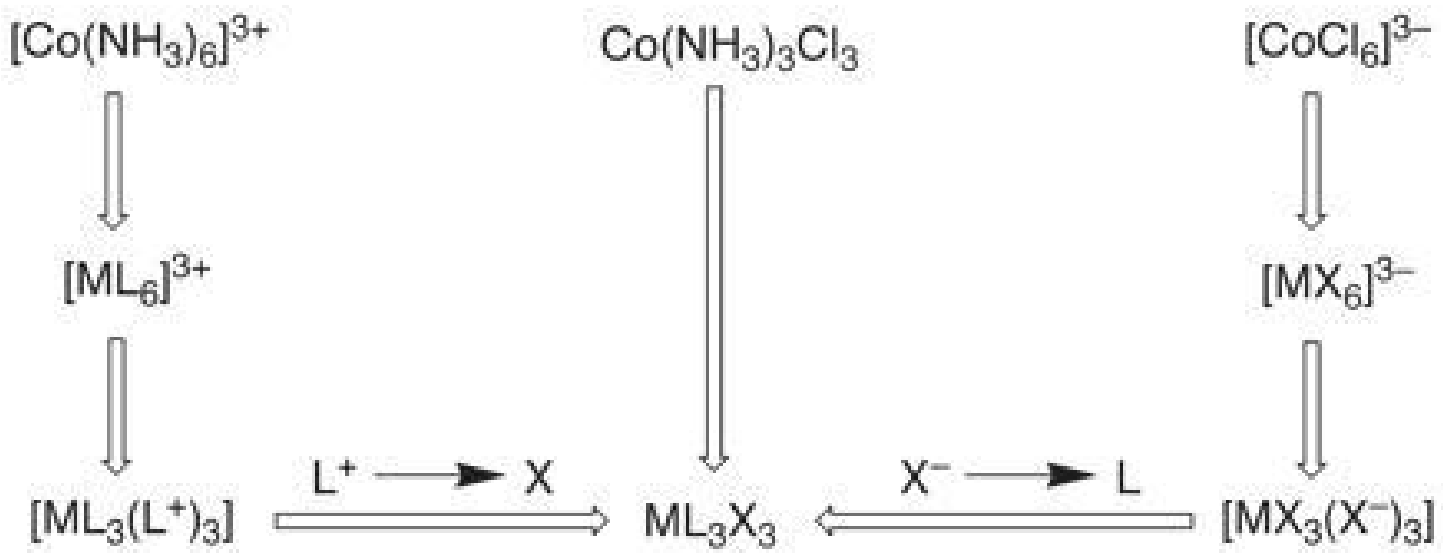
2 Cp	$[L_2X]_2$
2 H	X_2
ML_4X_4	



2 Cp	$[L_2X]_2$
3 H	X_3
$[ML_4X_5]^+$	
⇩	
ML_3X_6	

Convert Charged Species to Corresponding Neutral Class

For comparison purposes neutral classes are used



Important Definitions in the CBC Method

Table 1. Definitions pertaining to the CBC method.

Symbol	Definition
L	2-electron donor function
l	number of L functions
X	1-electron donor function
x	number of X functions
Z	0-electron donor function
z	number of Z functions
m	number of electrons on neutral metal
VN	valence number $VN = x + 2z$
LBN	ligand bond number $l + x + z$
EN	electron count $m + 2l + x$
d^n	number of electrons in "nonbonding" metal orbitals $n = m - x - 2z = m - VN$

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Example of an MLXZ Plot for Iron

Fe		Electron Number								
		10	11	12	13	14	15	16	17	18
Valence	0	ML		ML_2		ML_3		ML_4 <1%		ML_5 20%
	1		MLX		ML_2X		ML_3X		ML_4X <1%	
	2	MX_2		MLX_2		ML_2X_2 <1%		ML_3X_2 <1%		ML_4X_2 71%
	3		MX_3		MLX_3		ML_2X_3		ML_3X_3 <1%	
	4	MX_2Z		MX_4 <1%		MLX_4		ML_2X_4		ML_3X_4 7%
	5		MX_3Z		MX_5		MLX_5		ML_2X_5	
	6	MX_2Z_2		MX_4Z		MX_6		MLX_6		ML_2X_6 <1%
	7		MX_3Z_2		MX_5Z		MX_7		MLX_7	
	8	MX_2Z_3		MX_4Z_2		MX_6Z		MX_8		MLX_8 <1%

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Summary of Favored MLXZ

Comparison across the transition series

Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10
ScL_4X_3 (36%)	TiL_4X_4 (49%)	VL_6X (22%)	CrL_6 (48%)	MnL_5X (79%)	FeL_4X_2 (69%)	CoL_3X_3 (54%)	NiL_2X_2 (33%)
ScL_5X_3 (33%)	TiL_5X_3 (9%)	VL_4X_4 (16%)	CrL_5X_2 (24%)	MnL_4X_3 (12%)	FeL_5 (20%)	CoL_4X (34%)	NiL_3X_2 (26%)
ScL_3X_3 (10%)	TiL_2X_4 (7%)	VL_4X_3 (14%)	CrL_4X_4 (7%)	MnL_3X_5 (1%)	FeL_3X_4 (7%)	CoL_2X_5 (4%)	NiL_4 (16%)
YL_5X_3 (37%)	ZrL_4X_4 (55%)	NbL_5X_3 (32%)	MoL_5X_2 (40%)	TcL_5X (75%)	RuL_4X_2 (79%)	RhL_3X (41%)	PdL_2X_2 (81%)
YL_6X_3 (22%)	ZrL_5X_4 (25%)	NbL_6X (17%)	MoL_4X_4 (25%)	TcL_4X_3 (14%)	RuL_3X_4 (9%)	RhL_3X_3 (27%)	PdL_3X_2 (9%)
YL_4X_3 (19%)	ZrL_6X_2 (6%)	NbL_4X_5 (15%)	MoL_6 (19%)	TcL_3X_5 (2%)	RuL_5 (8%)	RhL_4X (22%)	PdL_3 (4%)
LaL_4X_3 (31%)	HfL_4X_4 (58%)	TaL_2X_5 (23%)	WL_5X_2 (34%)	ReL_5X (49%)	OsL_4X_2 (83%)	IrL_3X_3 (47%)	PtL_2X_2 (69%)
LaL_6X_3 (22%)	HfL_6X_2 (11%)	TaL_4X_5 (15%)	WL_4X_4 (27%)	ReL_4X_3 (29%)	OsL_5 (8%)	IrL_3X (26%)	PtL_2X_4 (11%)
LaL_3X_3 (17%)	HfL_5X_4 (8%)	TaL_5X_3 (14%)	WL_6 (15%)	ReL_3X_5 (4%)	OsL_3X_4 (7%)	IrL_4X (20%)	PtL_3 (9%)

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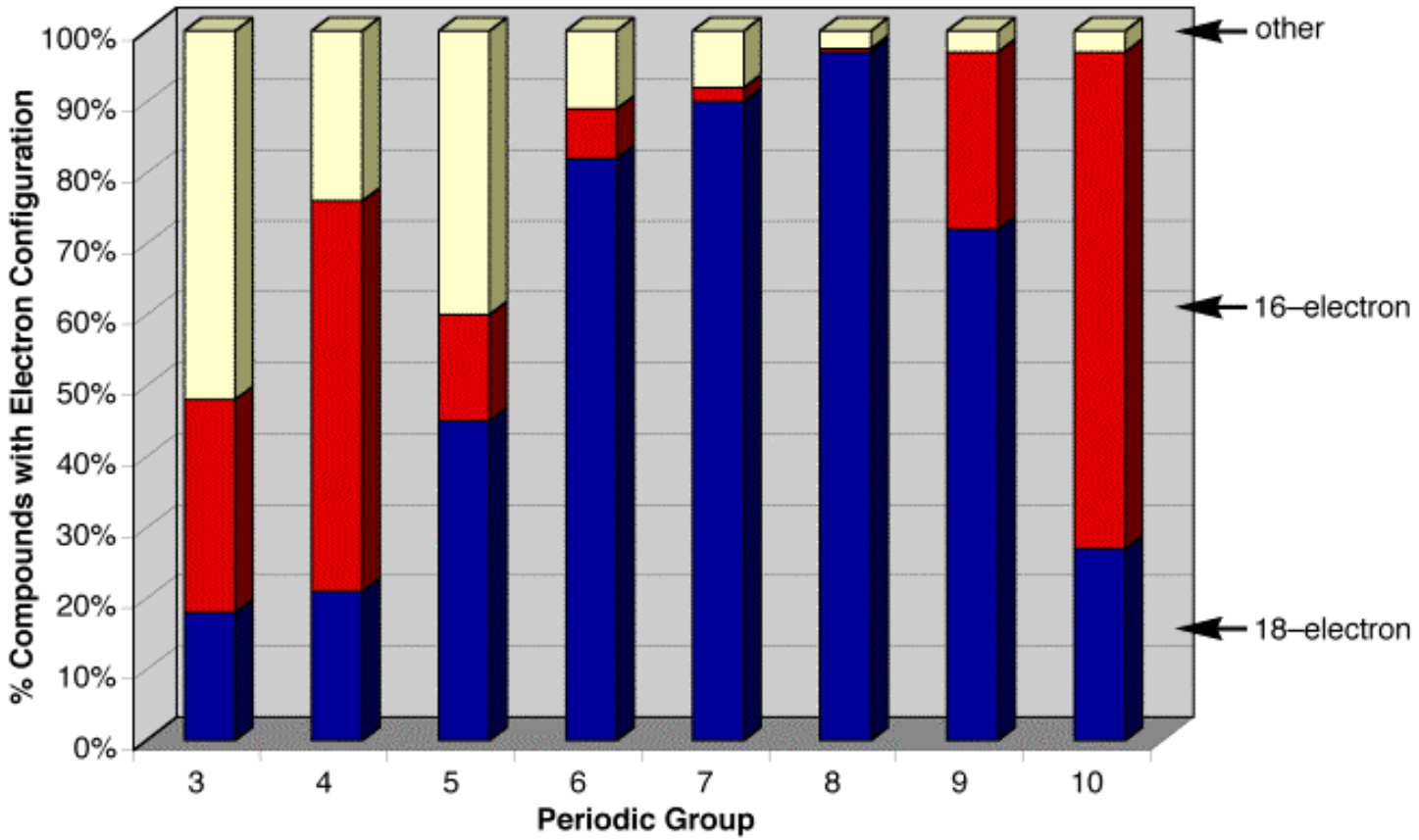
Examination of Trends

The 18 electron rule is more of a guideline



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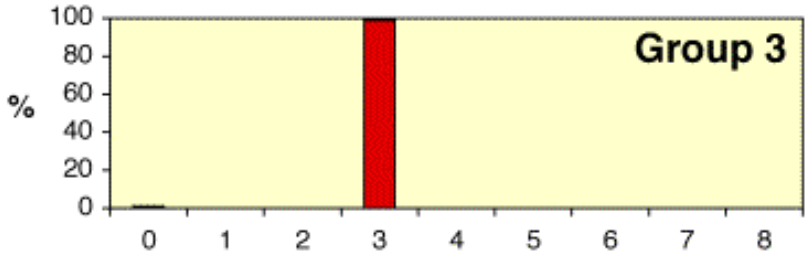
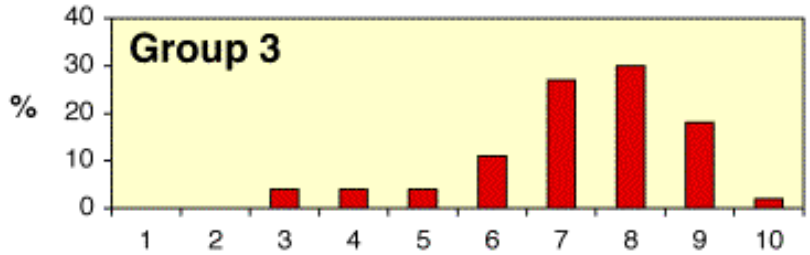
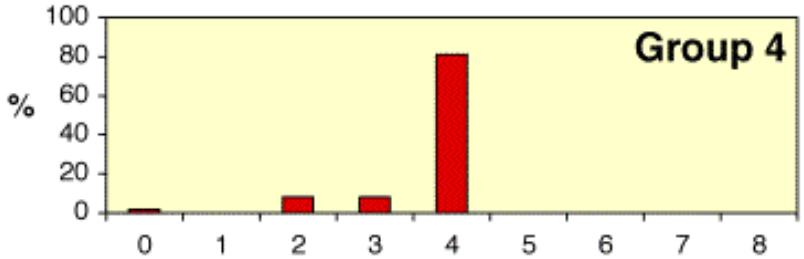
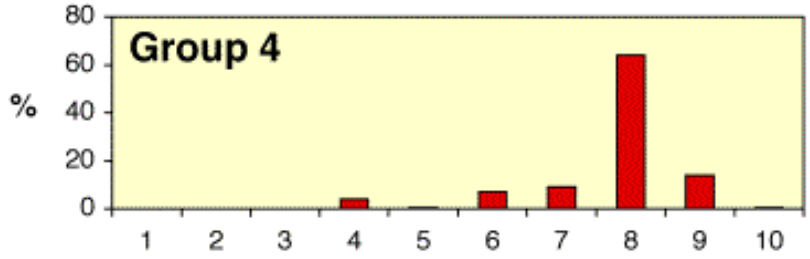
Trends in Valence and Ligand Bond Number

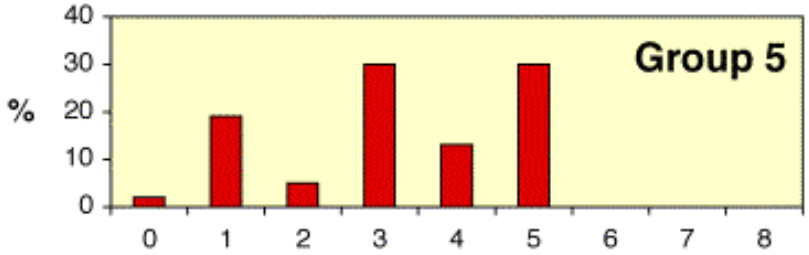
Groups 3-5

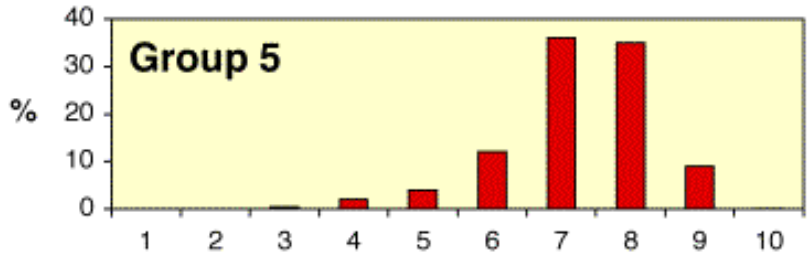












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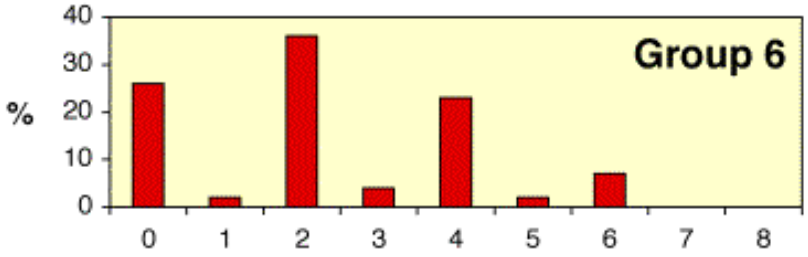
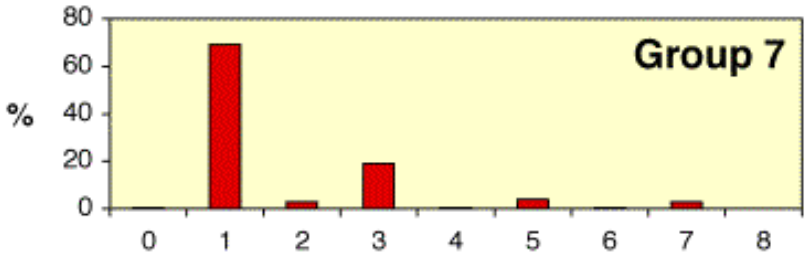
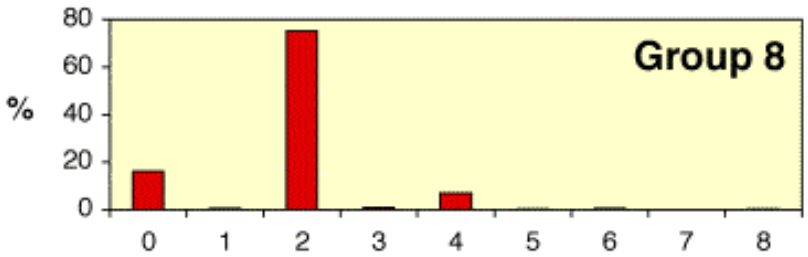
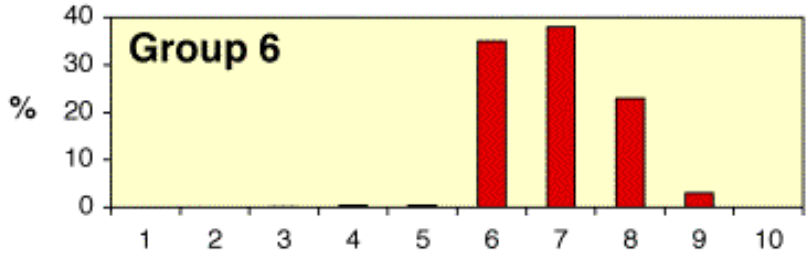
Trends in Valence and Ligand Bond Number

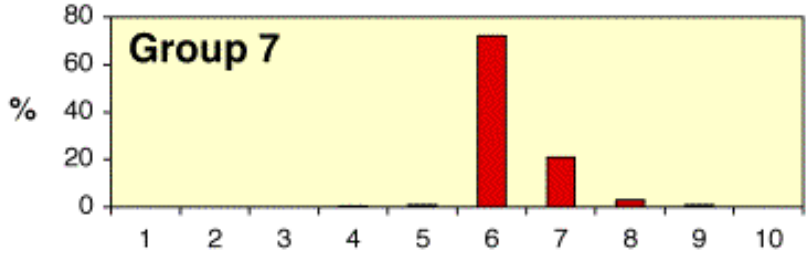
Groups 6-8

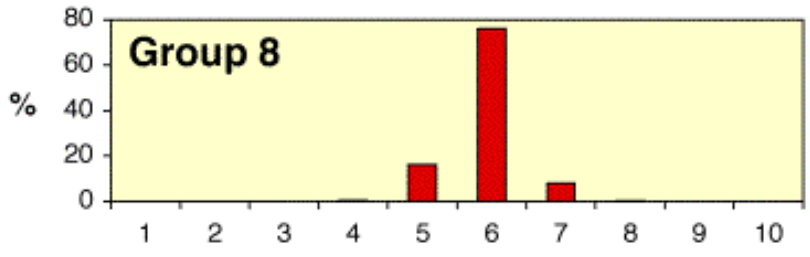












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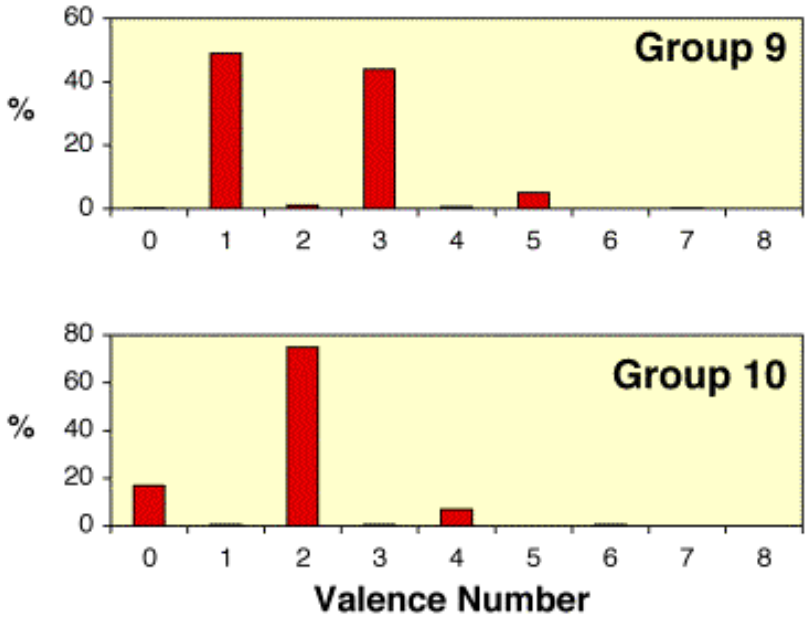
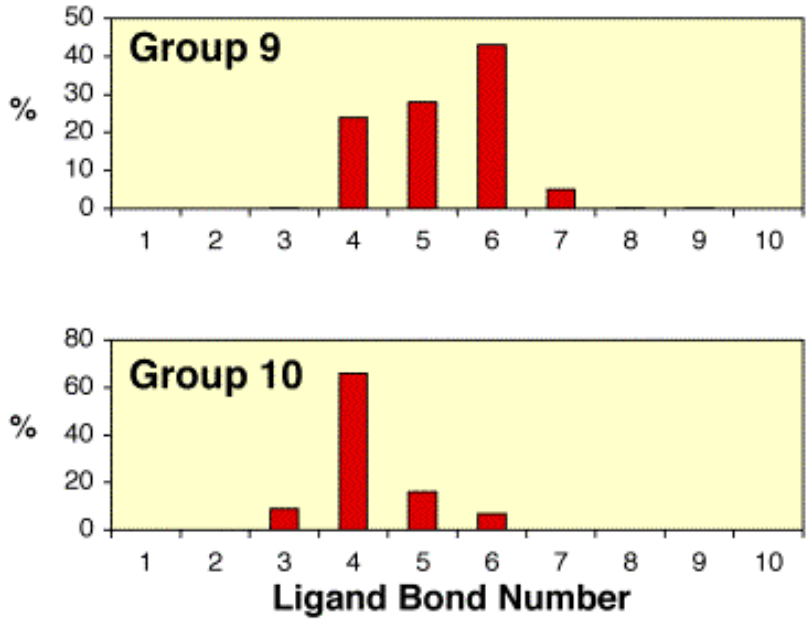
Trends in Valence and Ligand Bond Number

Groups 9-10





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- This web link lets you evaluate trends for the various d-block elements. Click here for mlxz plots
- Plots of $[ML_lX_xZ_z]$
- Electron Counts
- Valence distribution
- Ligand Bond Number distribution

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