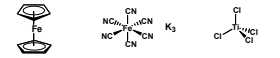
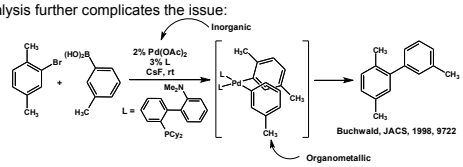
Ready; Catalysis — Organometallics: Definitions

Organometallics: Hard to define usefully and completely at the same time, but generally: Compounds containing metal-carbon bond(s).

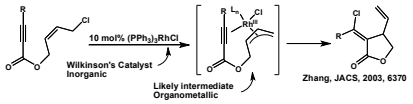


No question: Organometallic — ???? — No question: Inorganic

Catalysis further complicates the issue:



Buchwald, JACS, 1998, 9722



Zhang, JACS, 2003, 6370

Ready; Catalysis — Organometallics: Players

Organometallics is dominated by d electrons and orbitals

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Most commonly used in organometallic reactions

Usually d^0

Transition metals (copper often included)

p e- dominate

Usually have e- configuration $Xd^{10}(X+1)s^n$

Note: for our purposes, t.m.'s will be s^0

Ready; Catalysis — Organometallics: electronegativity

Pauling Electronegativity (ε)

H 2.2																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.4	F 4.0	Ne
Na 0.9	Mg 1.3											Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.1	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	S 2.5	Br 2.9	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.1	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.6	Sn 1.8	Sb 2.0	Te 2.1	I 2.6	Xe
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 2.3	Re 1.9	Os 2.2	Ir 2.2	Pt 2.3	Au 2.5	Hg 2.0	Tl 1.6	Pb 1.9	Bi 2.0	Po 2.0	At 2.2	Rn

Lanthanoids and Actinoids: 1.1 – 1.3

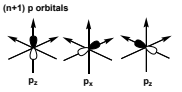
Alkali and main group, electronegativity *decreases* down the column
Transition metals: electronegativity *increases* down the column

Consider M-C bonds: Strength ~ $\frac{\text{Orbital overlap}}{\varepsilon M - \varepsilon C}$

T.M.-Carbon bond covalent, strong (note C-Pd less polarized than C-Si)
Alkali metal-Carbon bond largely ionic

Ready; Catalysis — Organometallics: bonding

(n+1) p orbitals



(n+1) s orbital

n d orbitals

lobes between axes — lobes on axes

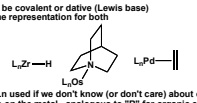
- Centrosymmetric
- Lobes 90° apart

- 9 orbitals, 9 bonds possible
- Hard to fit 9 ligands around most metals
- Usually up to 6 ligands, 3 non-bonding orbitals

Simple bonding:

σ

- Can be covalent or dative (Lewis base)
- Same representation for both

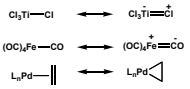


Note: Ln used if we don't know (or don't care) about other ligands on the metal - analogous to "R" for organic chemists

π

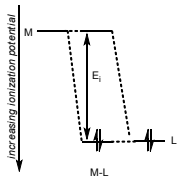
Covalent: 

Dative (metal can accept or donate e-)



Ready; Catalysis — Organometallics: bonding

Ionic Bonding: Driven by electrostatics



Strongest bond when high opposite charges interact.

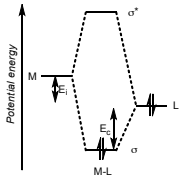
Charge differences are reflected in electronegativity differences.

Therefore large electronegativity differences give stronger bonds.

$E_i = f(-Q_M Q_L) = f[-(\varepsilon_M - \varepsilon_L)]$

ML bonding for early M is substantially ionic

Covalent Bonding: Driven by Overlap



Strongest covalent bond when orbitals of similar energy interact

Strength of interaction directly proportional to orbital overlap (matching size)

Strength of interaction inversely proportional to difference in electronegativity.

$E_c = f\left(\frac{\text{orbital overlap}}{\varepsilon_M - \varepsilon_L}\right)$

ML bonding for late M is substantially covalent

Ready; Catalysis — Organometallics: hard/soft

Soft Nucleophile → Hard Nucleophile

Increasing electronegativity

H 2.2																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.4	F 4.0	Ne
Na 0.9	Mg 1.3											Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.1	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	S 2.5	Br 2.9	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.1	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.6	Sn 1.8	Sb 2.0	Te 2.1	I 2.6	Xe
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 2.3	Re 1.9	Os 2.2	Ir 2.2	Pt 2.3	Au 2.5	Hg 2.0	Tl 1.6	Pb 1.9	Bi 2.0	Po 2.0	At 2.2	Rn

Hard electrophile → Soft electrophile

Increasing electronegativity

Increasing electrophilicity

Increasing electronegativity

Hard nucleophiles (i.e. ligands): Low E HOMO, high charge density
Hard electrophiles (i.e. metals): High E LUOM, high charge density
Hard-Hard interactions largely ionic (e.g. CsF)

Soft nucleophiles: High E HOMO, low charge density
Soft electrophiles: Low energy LUMO, low charge denisty
Soft-Soft interactions largely covalent (e.g. MeCu)

Ready; Catalysis | Organometallics: hard/soft

Hard/Soft effects on ligand binding

$$[M_{aq}]^n + X^- \rightleftharpoons[K_{eq}] [MX_{aq}]^{n-1}$$

$Log[K_{eq}]$

M^n	Ligand			
	F^-	Cl^-	Br^-	I^-
H^+	3	-7	-9	-9.5
Zn^{+2}	0.7	-0.2	-0.6	-1.3
Cu^{+2}	1.2	0.05	0.03	-
Hg^{+2}	1.0	6.7	8.9	12.9

Ready; Catalysis | Organometallics: ligands

ligands	charge	# e-
H, CR_3	-1	2
OR, NR_2, SR	-1	2
F, Cl, Br, I	-1	2
NR_3, PR_3, OR_2	0	2
	0	2
	-2	4
triplet (Schrock) carbene		
	0	2
singlet (Fischer) carbene		
	0	2
N-Heterocyclic Carbenes (NHC)		

ligands	charge	# e-
	0	2
	-1	4
M—CO or	0	2
	-1	6
	0	6
	-2	4
η-2 peroxo		
	-1	2
superoxide		
	-2	4
terminal oxo		
BF_4, SbF_6, $B(C_6F_5)_4$ $B[C_6H_3\text{-}(CF_3)_2]_4$, OTf	-1	~0

Ready; Catalysis | Organometallics: phosphines

On Phosphines

Strong σ-donors

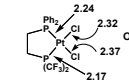
M PR_3

σ-donation

$PCl_3 < P(OR)_3 < PPh_3 < PR_3$

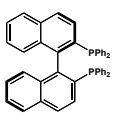
Strong π-acceptors

$d_M \rightarrow d_P$ or $dM \rightarrow \sigma^*_{P\text{-}R}$

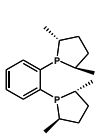


Orpen Chem. Com. 1985, 1310

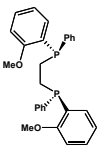
Chiral and modular



BINAP

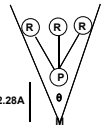


DuPhos



DIPAMP

Cone Angle



ligand	θ
PF_3	104
$P(OMe)_3$	107
PMe_3	118
$PPhMe_2$	122
dppe	125
PEt_3	132
PPh_3	145
PCy_3	170
$P(tBu)_3$	182
H	75
Me	90
CO	95
Cp	136

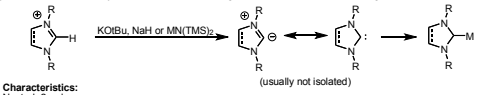
toleman
Chem Rev. 1977,313

Ready; Catalysis — Organometallics: NHC's

N-Heterocyclic Carbenes (NHC's)

Reviews: Herrmann, *ACIEE*, **2002,** 1290; Ogan, *ACIEE*, **2007,** 2768

Key initial discoveries: Bulky NHC's are stable: Arduengo, *JACS*, **1991,** 361. Useful as ligands: Herrmann, *ACIEE*, **1995**, 2371



Characteristics:

Neutral, 2e- donor

Strong σ-donor (similar to phosphine)

Weak π acceptor

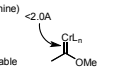
Modular

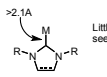
M(NHC) complexes:

often air stable

thermally and hydrolytically stable

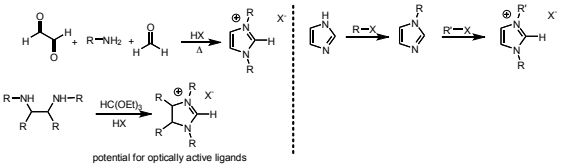
e- rich





Little backbonding - similar to olefin see Bielawski, JACS, 2006, 16514

Synthesis: 3 common methods (see Herrman review)

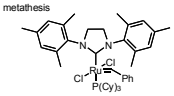


potential for optically active ligands

Ready; Catalysis — Organometallics: NHC's

Applications:

Olefin metathesis

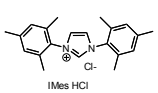


Grubb's 2nd generation catalyst

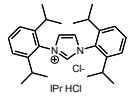
Almost all Pd-catalyst reactions work using NHCs.
Heck, Suzuki, Stille, Buchwald-Hartwig, Sonagashira...

Ni, Fe and Ir chemistry also reported. Like with phosphines, best ligand is case-dependent.

Two most popular NHC precursors: (bulky NAr to prevent dimer formation)



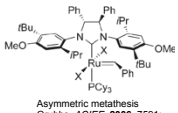
IMes HCl



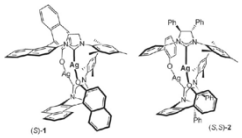
IPr HCl

Optically active versions have been made

For asymmetric hydrogenation
Burgess, *JACS*, **2001,** 8878



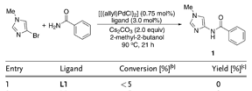
Asymmetric metathesis
Grubbs, *ACIEE*, **2006**, 7591; *JACS*, **2006**, 1840



Conjugate addition
Hoveyda, *ACIEE*, **2007**, 1097

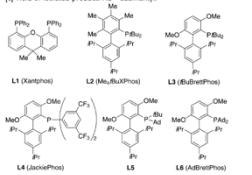
Ligand Identity Can Dictate Reaction Efficiency

A typical case: Buchwald, *ACIE*, **2012**, 4710

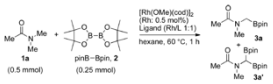


Entry	Ligand	Conversion [%][a]	Yield [%][b]
1	**L1**	< 5	0
2	**L2**	< 5	0
3	**L3**	35	15
4	**L4**	< 5	0
5	**L5**	43	24
6	**L6**	100	83

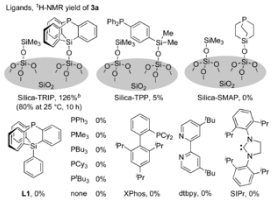
[a] Reaction conditions: 4-bromo-1-methylimidazole (0.5 mmol), benzamide (1 mmol), [[(allyl)PdCl]2] (0.75 mol %), ligand (3 mol %), Cs_2CO_3 (1 mmol), 2-methyl-2-butanol (1 mL), 90 °C, 21 h. [b] Determined by GC. [c] Yield of isolated product. Ad = adamantyl.



An extreme case: Sawamura, *JACS*, **2012**, 12924

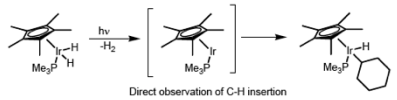


Ligands, ^{1}H-NMR yield of **3a**



Ready; Catalysis — Organometallics: Bond Strength

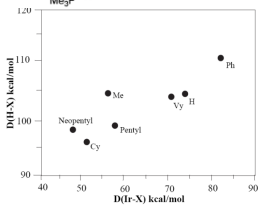
Background:



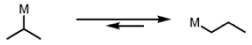
Direct observation of C-H insertion
Bergman, JACS, 1982, 352

Determination of relative M-X bond strengths

Bergman
Polyhedron, 1988, 1429



Conclusions:
M-C bond strength correlates with H-C bond strength
CH_3>1°>2°>3°
$sp > sp^2 > sp^3$



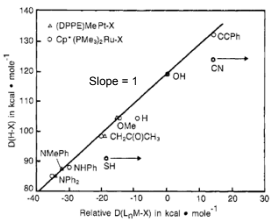
Ready; Catalysis — Organometallics: Bond Strength

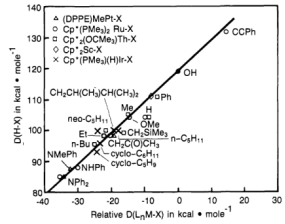
Bryndza, Bercaw et al. JACS, 1987, 1444 Observed experimentally:

$L_nM{-}X + H{-}Y \rightleftharpoons ML_n{-}Y + H{-}X$ $\quad K_{eq} \sim 1$

eg

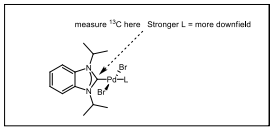
$Cp^*(PMe_3)_3RuOH + CH_3COCH_3 \rightleftharpoons Cp^*(PMe_3)_3RuCH_2COCH_3 + H_2O \quad K_{eq} = 2.3$



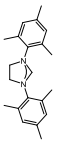


Exceptions: M-H (5-15 kcal too strong)
M-OR too strong in d^0
M-S, M-Si too strong in late TM's. But:

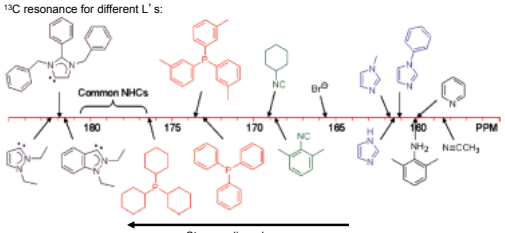
Ready; Catalysis — Organometallics: Bond Strength, neutral ligands



representative 'common NHC'
aka SIMes, found in Grubbs II
176 ppm on this chart



^{13}C resonance for different L's:

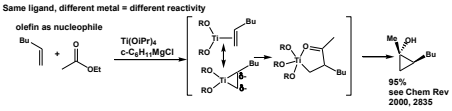


Stronger ligand

Huynh, *Organomet.* **2009**, 5395

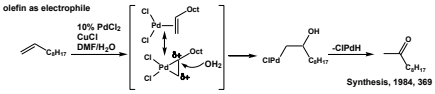
Same ligand, different metal = different reactivity

olefin as nucleophile



95%
see Chem Rev
2000, 2835

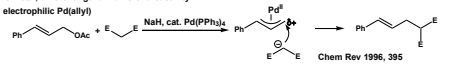
olefin as electrophile



Synthesis, 1984, 369

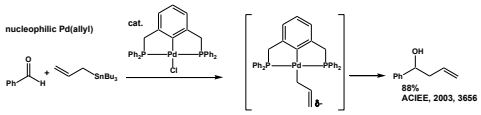
Same metal, different ligand = different reactivity

electrophilic Pd(allyl)

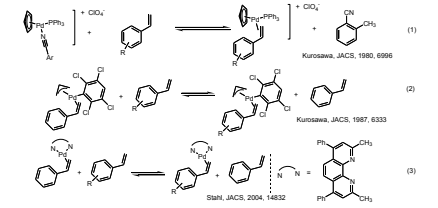


Chem Rev 1996, 395

nucleophilic Pd(allyl)



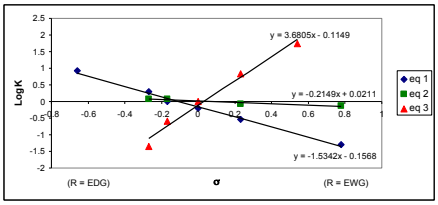
88%
ACIEE, 2003, 3656



(1) Kurosawa, JACS, 1980, 6996

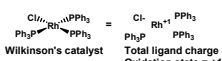
(2) Kurosawa, JACS, 1987, 6333

(3) Stahl, JACS, 2004, 14832



Electron Counting and Oxidation State

1. Decide what charge a ligand has
2. Determine # e⁻s donated
3. Assume Metal has charge equal in magnitude, opposite in charge to sum of ligands
4. Oxidation state = charge on metal
5. d e- count = #e- for neutral element – charge
6. Total e- count = d e- + sum of ligand electrons
7. 18 e- is stable # of e- (nobel gas configuration), 16 e- for square planar

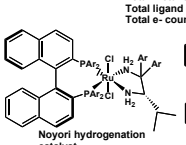


Wilkinson's catalyst

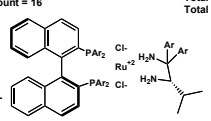
Total ligand charge = -1
Oxidation state = +1
Total metal e- = 8
Total ligand e- = 8
Total e- count = 16

Zeise's salt

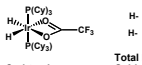
Total ligand charge = -2
Oxidation state = +2
Total metal e- = 8
Total ligand e- = 8
Total e- count = 16



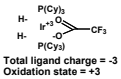
Noyori hydrogenation catalyst



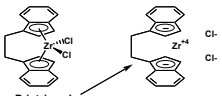
Total ligand charge = -2
Oxidation state = +2
Total metal e- = 6
Total ligand e- = 12
Total e- count = 18



Crabtree's dehydrogenation catalyst

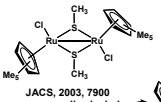


Total ligand charge = -3
Oxidation state = +3
Total metal e- = 6
Total ligand e- = 12
Total e- count = 18

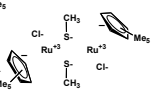


Brintzinger's ligand

Total ligand charge = -4
Oxidation state = +4
Total metal e- = 0
Total ligand e- = 16
Total e- count = 16



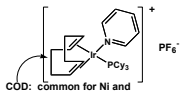
JACS, 2003, 7900
propargylic alcohol substitution



Cp* (Cp star)

Total ligand charge = -3
Oxidation state = +3
Total metal e- = 5
Ru-Ru bond = 1e-/Ru
Total ligand e- = 12
Total e- count = 18

Note: electron count same for each Ru b/c they are equivalent



COD: common for Ni and hydrogenation cat (why?)

Crabtree catalyst (homogeneous hydrogenation)

Total ligand charge = -1
Oxidation state = +1
Total metal e- = 8
PF6 contribution = 0
Total ligand e- = 8
Total e- count = 16

Geometries of transition metal complexes
Balance between sterics (maximum ligand separation) and electonics (minimum filled antibonding, evenly distibuted nb)

For MO treatment, see Albright, Tetrahdron, 1982, 1339.

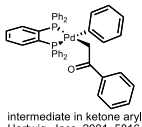
Octahedral
most common geometry
for ML6; often 18e-, often for d6

first eg of H_2 η^2-complex
jacs 1984, 451

Tetrahedral
Common for d10, d4 and d0
sterically best way for ML4

aka "tetrakis"
probably most common Pd source

Square Planar
very common for d8 metals
16e- very stable (17th e- would be antibonding)



intermediate in ketone arylations
Hartwig, Jacs, 2001, 5816

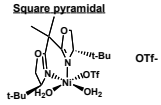
Geometries of transition metal complexes, cont.

Some less common geometries

Trigonal bipyramidal

Note both are ML5, 18e- complexes of d8 metals

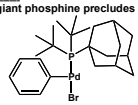
Square pyramidal



OTf-

asymmetric aldol catalyst
evans, Jacs, 2003, 8706

Bent
giant phosphine precludes 4th ligand



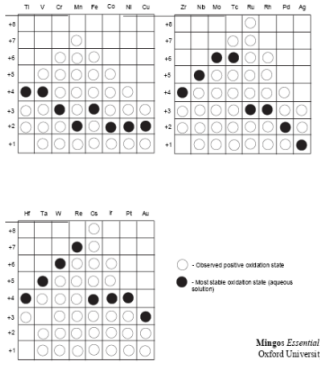
Hartwig, Jacs, 2002, 9346

Linear
common for Cu, Ag and Au

For a list of geometry by metal and oxidations state, see Jeffrey Moore's web site:
http://sulfur.scs.uiuc.edu/

Ready; Catalysis — Organometallics: Oxidation States

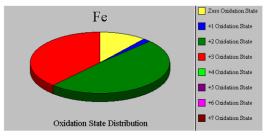
Transition metals are such good catalysts because they can change oxidation states:

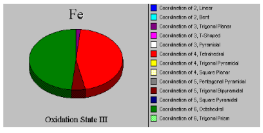


Mingos *Essential Trends in Inorganic Chemistry*; Oxford University Press, 1998.

Ready; Catalysis — Organometallics: Oxidation States

A useful reference, and fun for the whole family:
Web page for Jeffrey S. Moore (U. Illinois, chemistry)
http://sulfur.scs.uiuc.edu/
Under the 'periodic table' link





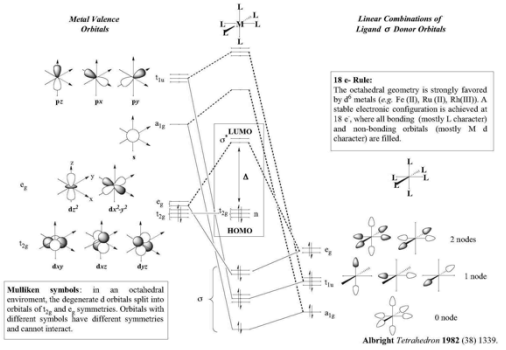
Experimental Results	
Zero Oxidation State	17
+1 Oxidation State	3
+2 Oxidation State	77
+3 Oxidation State	60
+4 Oxidation State	0
+5 Oxidation State	0
+6 Oxidation State	0
+7 Oxidation State	0

Experimental Results	
Coordination of 2, Linear	0
Coordination of 2, Bent	0
Coordination of 3, Trigonal Planar	1
Coordination of 3, T-Shaped	0
Coordination of 3, Pyramidal	0
Coordination of 4, Tetrahedral	27
Coordination of 4, Trigonal Pyramidal	0
Coordination of 4, Square Planar	0
Coordination of 5, Pentagonal Pyramidal	0
Coordination of 5, Trigonal Bipyramidal	3
Coordination of 5, Square Pyramidal	0
Coordination of 6, Octahedral	29
Coordination of 6, Trigonal Prism	0

I stole the next 3 slides!!!

M.C. White, *Chem 153* — Structure & Bonding -15- — Week of September 17, 2002

MO Description of σ bonding in ML_6



18 e- Rule: The octahedral geometry is strongly favored by d^6 metals (e.g. Fe (II), Ru (II), Rh(III)). A stable electronic configuration is achieved at 18 e-, where all bonding (mostly L character) and non-bonding orbitals (mostly M d character) are filled.

Mulliken symbols: in an octahedral enviroment, the degenerate d orbitals split into orbitals of t_{2g} and e_g symmetries. Orbitals with different symbols have different symmetries and cannot interact.

Albright *Tetrahedron* **1982** (38) 1339.

MO Description of σ bonding in ML_4 square planar