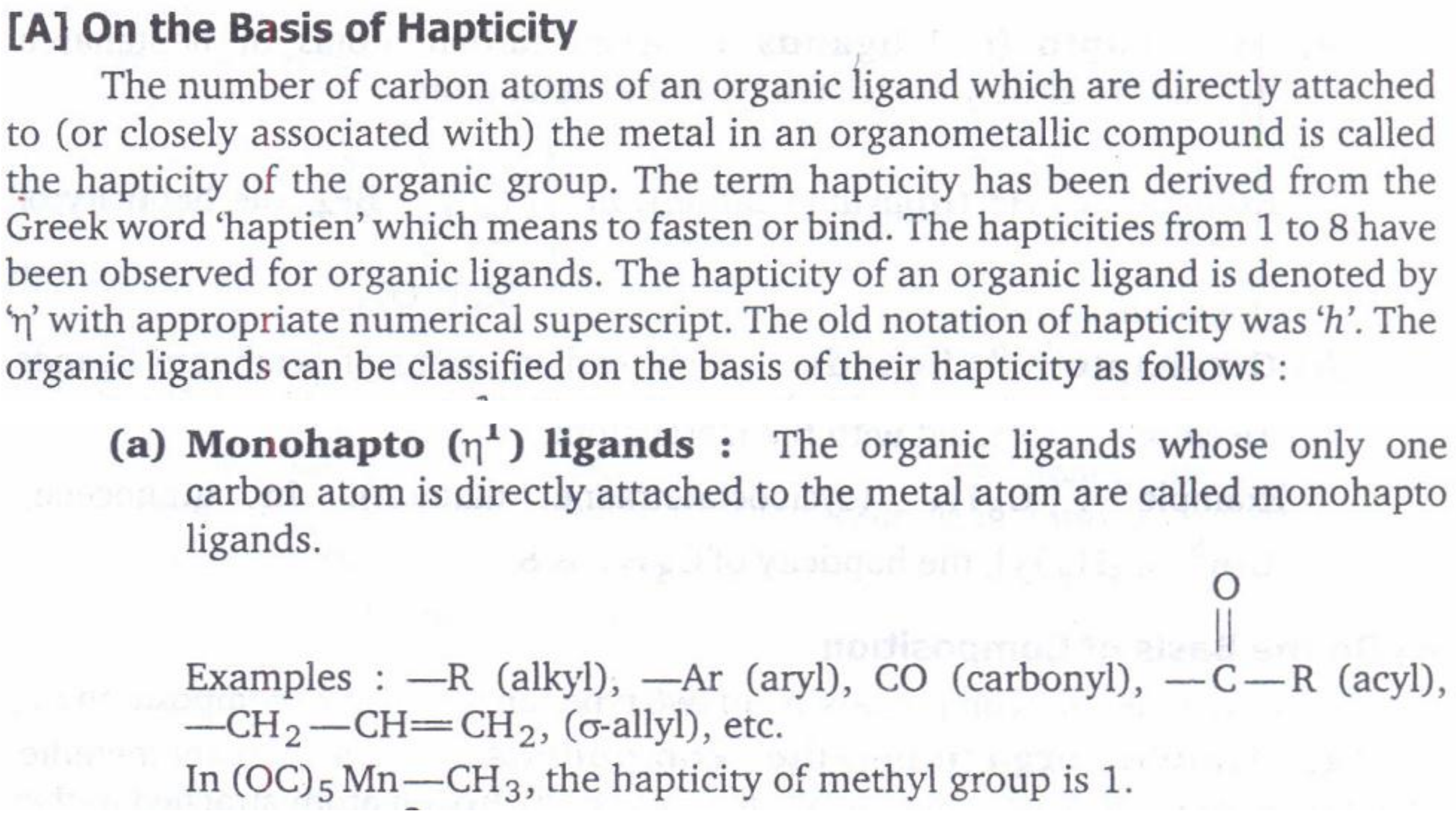
Classification of organometallic compounds

The organometallic compounds can be classified in a number of ways as mentioned below:



[A] On the Basis of Hapticity

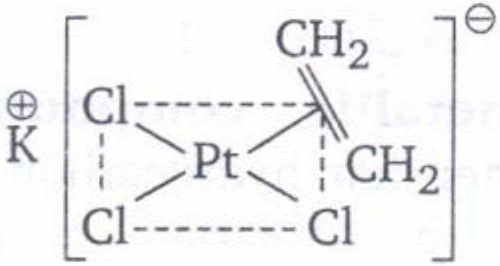
The number of carbon atoms of an organic ligand which are directly attached to (or closely associated with) the metal in an organometallic compound is called the hapticity of the organic group. The term hapticity has been derived from the Greek word 'haptien' which means to fasten or bind. The hapticities from 1 to 8 have been observed for organic ligands. The hapticity of an organic ligand is denoted by 'η' with appropriate numerical superscript. The old notation of hapticity was '*h*'. The organic ligands can be classified on the basis of their hapticity as follows :

(a) Monohapto (η^1) ligands : The organic ligands whose only one carbon atom is directly attached to the metal atom are called monohapto ligands.

Examples : —R (alkyl), —Ar (aryl), CO (carbonyl), $-\overset{\overset{\displaystyle O}{\|}}{C}-R$ (acyl), $-CH_2-CH{=}CH_2$, (σ-allyl), etc.

In $(OC)_5Mn-CH_3$, the hapticity of methyl group is 1.

(b) Dihapto (η^2) ligands : The organic ligands whose two carbon atoms are closely associated with the metal atom are called dihapto ligands. Example : $CH_2{=}CH_2$ (ethylene) and other alkenes.



In the Zeise's salt, the hapticity of ethylene is 2.

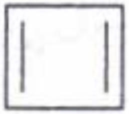
(c) Trihapto (η^3) ligands : In such ligands, three carbon atoms are closely associated with the metal atom.

Example :

(π - allyl)

The π-allyl group is represented by . In (OC)$_4$ Mn , the hapticity of π-allyl group is 3.

(d) **Tetrahapto (η^4) ligands :** Four carbon atoms of such ligands are closely associated with the metal atom.

Example :  (cyclobutadiene). In  Fe$(CO)_3$, the hapticity of cyclobutadiene is 4.

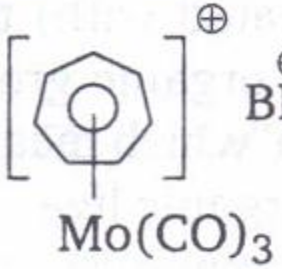
(e) **Pentahapto (η^5) ligands :** Five carbon atoms of pentahapto ligands are closely associated with the metal atom.

Example : C_5H_5 (cyclopentadienyl). In ferrocene, $[Fe(\eta^5-C_5H_5)_2]$, the hapticity of C_5H_5 is 5.

(f) **Hexahapto (η^6) ligands :** Six carbon atoms of hexahapto ligands are closely associated with the metal atom.

Example : C_6H_6 (benzene). In bis (benzene) chromium (o), *i.e.*, $[Cr(\eta^6-C_6H_6)_2]$, the hapticity of C_6H_6 is 6.

(g) Heptahapto (η^7) ligands : Seven carbon atoms of heptahapto ligands are closely associated with the metal atom.

Example : $C_7\overset{\oplus}{H}_7$ (tropylium cation). In  $B\overset{\ominus}{F}_4$, the hapticity of tropylium cation is 7.

(h) Octahapto (η^8) ligands : Eight carbon atoms of octahapto ligands are closely associated with the metal atom.

Example : $C_8\overset{\ominus\ominus}{H}_8$ (cyclooctatetraene dianion). In uranocene, $[U(\eta^8-C_8H_8)_2]$, the hapticity of $C_8\overset{\ominus\ominus}{H}_8$ is 8.

[B] On the Basis of Composition

The organometallic compounds are of two types on the basis of composition :

(a) Simple organometallic compounds : The organometallic compounds which have only hydrocarbon radical or hydrogen atom attached to the metal atom are called simple organometallic compounds. Example : $(CH_3)_4Pb$, $(CH_3)_3SnH$, etc. The simple organometallic compounds are further of two types :

(i) Symmetrical, *e.g.*, $(CH_3)_2Cd$

(ii) Unsymmetrical, *e.g.*, $CH_3ZnCH_2CH_3$

(b) Mixed organometallic compounds : The organometallic compounds in which groups other than hydrocarbon radicals or hydrogen atom are also directly attached to the metal atom are called mixed organometallic compounds. Example : CH_3MgBr, $(CH_3)_2SnCl_2$, etc.

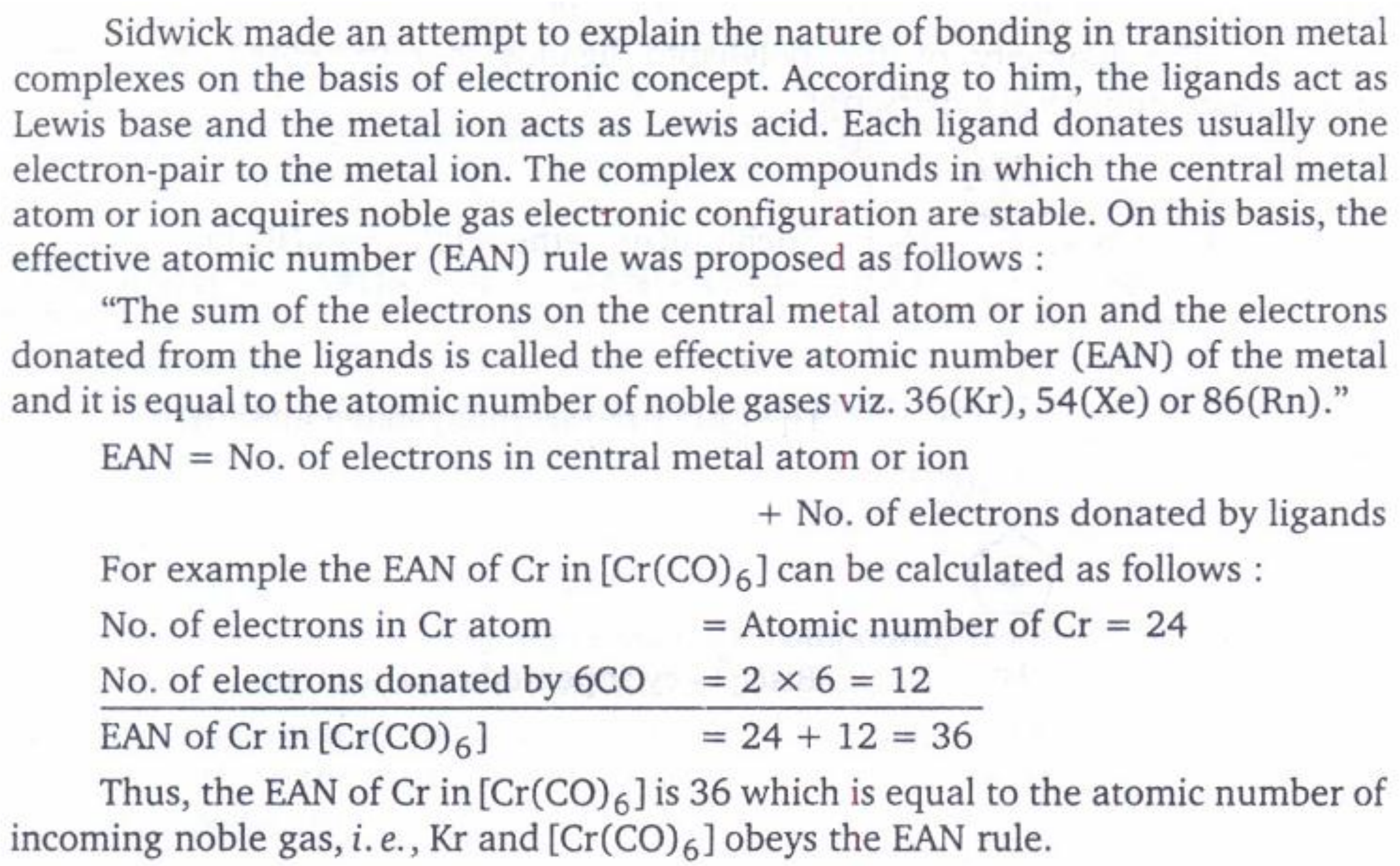
[C] On the Basis of Position of Metal in the Periodic Table

The organometallic compounds are of two types on the basis of position of the metal in the periodic table.

(a) Main group organometallic compounds : The organometallic compounds formed by *s*-block and *p*-block elements are called main group organometallic compounds. Example : CH_3Li (methyllithium), CH_3MgBr (methyl magnesium bromide), $(CH_3)_4Pb$ (tetramethyllead), etc.

(b) *d*- and *f*-block organometallic compounds : The organometallic compounds formed by *d*- and *f*-block elements are called *d*- and *f*-block organometallic compounds. Examples : $[Fe(\eta^5-C_5H_5)_2]$ (ferrocene), $[U(\eta^8-C_8H_8)_2]$ (uranocene), etc.

18-Electron Rules



Sidwick made an attempt to explain the nature of bonding in transition metal complexes on the basis of electronic concept. According to him, the ligands act as Lewis base and the metal ion acts as Lewis acid. Each ligand donates usually one electron-pair to the metal ion. The complex compounds in which the central metal atom or ion acquires noble gas electronic configuration are stable. On this basis, the effective atomic number (EAN) rule was proposed as follows :

"The sum of the electrons on the central metal atom or ion and the electrons donated from the ligands is called the effective atomic number (EAN) of the metal and it is equal to the atomic number of noble gases viz. 36(Kr), 54(Xe) or 86(Rn)."

EAN = No. of electrons in central metal atom or ion + No. of electrons donated by ligands

For example the EAN of Cr in $[Cr(CO)_6]$ can be calculated as follows :

No. of electrons in Cr atom = Atomic number of Cr = 24

No. of electrons donated by 6CO $= 2 \times 6 = 12$

EAN of Cr in $[Cr(CO)_6]$ $= 24 + 12 = 36$

Thus, the EAN of Cr in $[Cr(CO)_6]$ is 36 which is equal to the atomic number of incoming noble gas, *i.e.*, Kr and $[Cr(CO)_6]$ obeys the EAN rule.

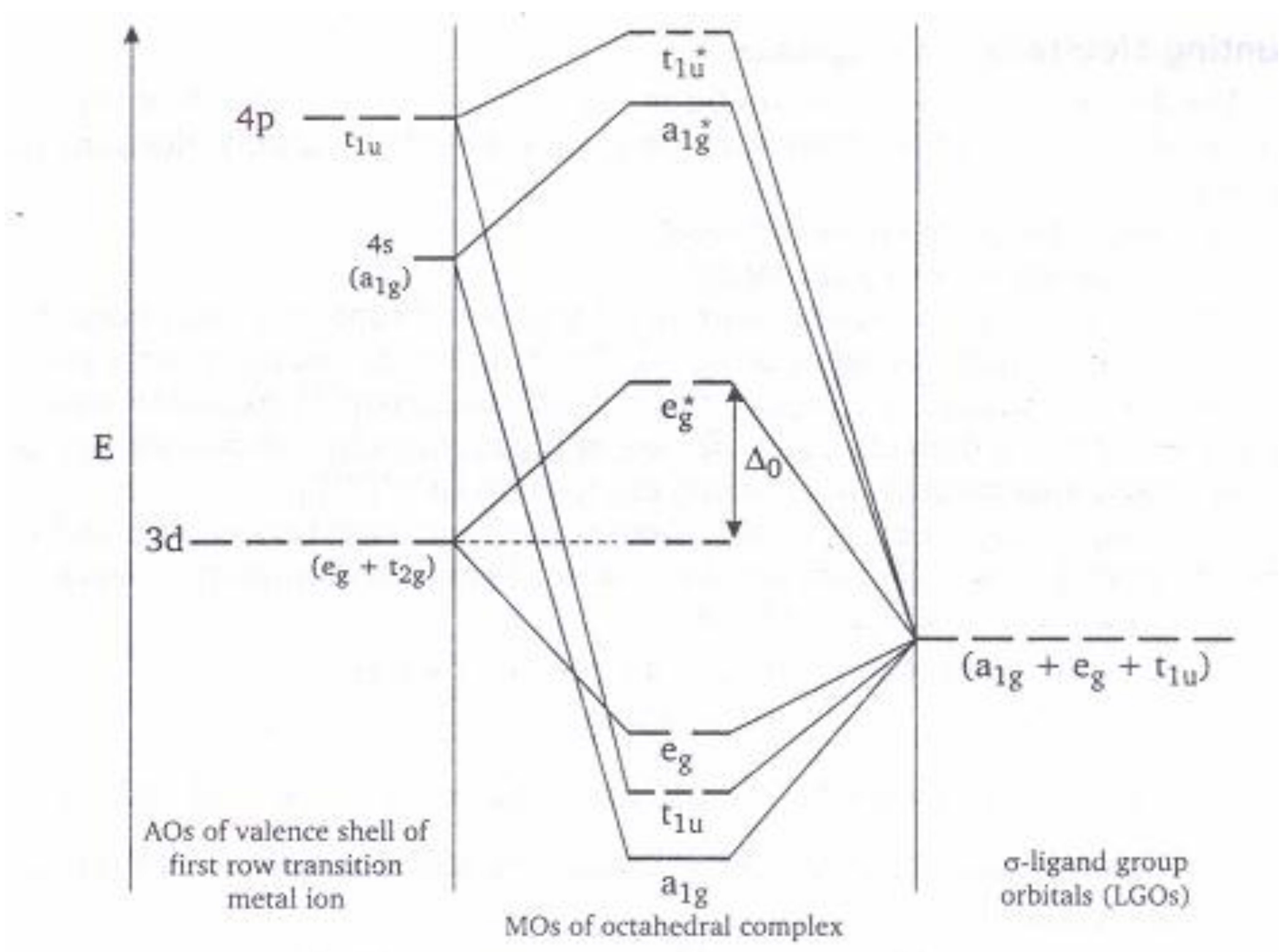

E
4p
t_{1u}
4s
(a_{1g})
3d
$(e_g + t_{2g})$
t_{1u}^*
a_{1g}^*
e_g^*
Δ_0
e_g
t_{1u}
a_{1g}
$(a_{1g} + e_g + t_{1u})$
AOs of valence shell of first row transition metal ion
MOs of octahedral complex
σ-ligand group orbitals (LGOs)

Figure 1.1

If the ligands have vacant antibonding $\pi*$ molecular orbitals or vacant AOs, t_{2g} orbitals of the metal ion are stabilized by metal → ligand π-bonding as shown in fig 1.2.

It is obvious from the these diagrams that total 18-electrons are required to fill up all the nine bonding molecular orbitals viz., a_{1g}, t_{1u}, e_g and t_{2g} (in the case of no metal → ligand π bonding t_{2g} orbitals remain non-bonding) and the extent of bonding will be maximum if 18-electrons are present in these molecular orbitals. These electrons are contributed from the central metal ion and ligands. The occupation of antibonding e_g^* MOs is not favourable energetically because it would lead to increase in the energy and decrease in the stability of the complex.

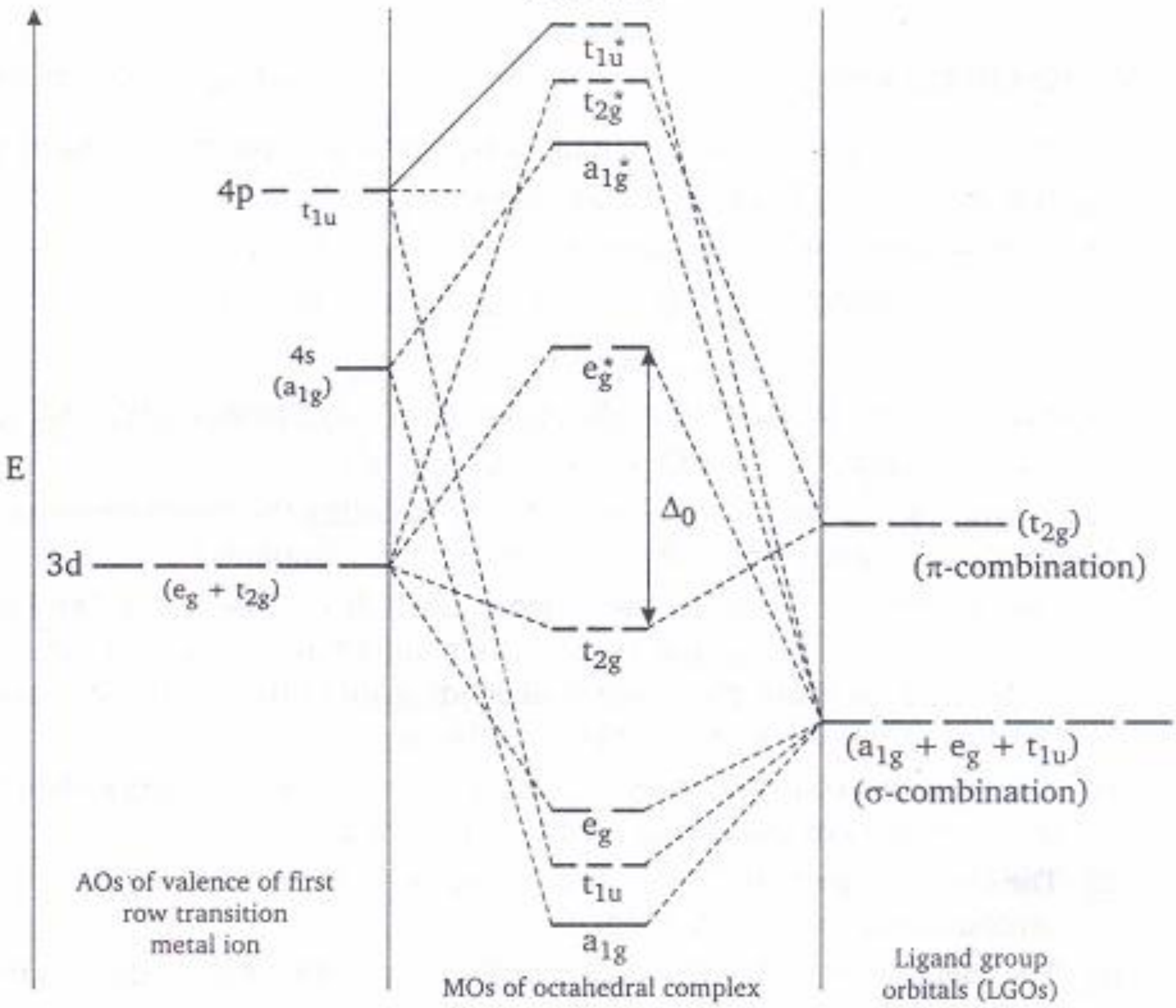

t_{1u}^*
t_{2g}^*
a_{1g}^*
4p
t_{1u}
4s
(a_{1g})
e_g^*
E
Δ_0
(t_{2g})
(π-combination)
3d
$(e_g + t_{2g})$
t_{2g}
$(a_{1g} + e_g + t_{1u})$
(σ-combination)
e_g
t_{1u}
a_{1g}
AOs of valence of first row transition metal ion
MOs of octahedral complex
Ligand group orbitals (LGOs)

Figure 1.2

Counting Electrons in Complexes

The 18-electron rule is very useful in predicting stabilities and structures of organometallic compounds. There are two conventions for counting electrons in complexes

(a) Neutral atom or covalent model

(b) Oxidation state or ionic model

Both the conventions have almost equal number of supporters and both the methods lead to exactly the same net result. The covalent model is probably more foolproof because it does not require the correct assignment of oxidation states, which is sometimes a difficult job in the case of organometallic compounds. Let us illustrate above two methods by counting electrons in $HCo(CO)_4$.

According to the covalent model, there is covalent bond between Co and H atoms in $HCo(CO)_4$ and H atom acts as 1*e* donor ligand. Accordingly, number of electrons in the valence orbitals of Co in

$$\begin{aligned} HCo(CO)_4 &= 9(Co) + 4 \times 2(CO) + 1 \times 1(H) \\ &= 9 + 8 + 1 = 18 \end{aligned}$$

According to the ionic model, there is ionic bond between $(OC)_4\overset{\oplus}{Co}$ and $\overset{\ominus}{H}$ ions in $HCo(CO)_4$ and $\overset{\ominus}{H}$ ion acts as $2e^-$ donor ligand. Therefore, number of electrons in the valence orbitals of Co in

$$\begin{aligned} HCo(CO)_4 &= 8(Co^+) + 4 \times 2(CO) + 1 \times 2(H^-) \\ &= 8 + 8 + 2 = 18 \end{aligned}$$

No scientist has suggested the electron counting in $HCo(CO)_4$ by considering ionic bonding between $\overset{\oplus}{H}$ and $\overset{\ominus}{Co}(CO)_4$ ions in which $\overset{\oplus}{H}$ ion acts as zero electron donor and cobalt is in – I oxidation state as follows :

Number of electrons in the valence orbitals of cobalt in

$$\begin{aligned} HCo(CO)_4 &= 10(Co^-) + 4 \times 2(CO) + 1 \times 0(H^+) \\ &= 10 + 8 = 18 \end{aligned}$$

It is quite surprising because the acidification of $Co(C\overset{\ominus}{O})_4$ produces $HCo(CO)_4$.

$$NaCo(CO)_4 + HCl \longrightarrow NaCl + HCo(CO)_4$$

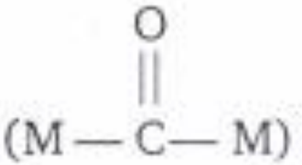
The following steps are generally followed for counting the electrons present in the valence shell of central metal in an organometallic compound :

(i) The electrons present in the valence shell [*i.e.*, $(n-1)d$, ns and np orbitals] of the central metal atom are counted and then electrons are added to it or subtracted from it depending upon the nature of charge (positive or negative) present on it in the complex.

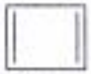
(ii) The electrons contributed by the organic ligands to the valence shell of central metal are counted as mentioned in table 1.2.

(iii) The electrons donated by the conventional ligands to the valence shell of central metal are also counted.

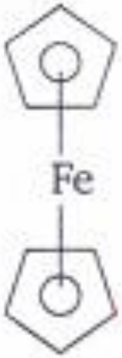
(iv) The metal-metal (M—M) bond contributes one electron to the valence shell of each metal atom.

(v) The bridging carbonyl group ( $M-\overset{\overset{O}{\|}}{C}-M$) contributes one electron to the valence shell of each metal atom attached by it.

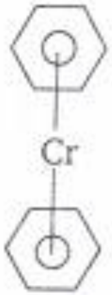
(vi) The electrons counted in steps (i) to (v) are added to find out the total number of electrons in the valence shell of the central metal of a complex compound.

Ligand	**Hapticity**	**Available electrons**	
		Covalent model	**Ionic model**
$-CH_3$ (Methyl)	η^1	1	2
$CH_2=CH-CH_2-$ (σ-Allyl)	η^1	1	2
$CH_2=CH_2$ (Ethene)	η^2	2	2
 (π-Allyl)	η^3	3	4
 (1, 3-Butadiene)	η^4	4	4
 (Cyclobutadiene)	η^4	4	4
 (Cyclopentadienyl)	η^5	5	6
 (Benzene)	η^6	6	6
 (Tropylium cation)	η^7	6	6
 (Cyclooctatetraene dianion) or Cyclooctatetraenide ion	η^8	10	10

Illustrative Examples of Electron Counts :

	Complex/Organometallic compound	**Electron count**			
		Ionic model		**Covalent model**	
(i)	$HMn(CO)_5$	Mn^+	6*e*	Mn	7*e*
		H^-	2*e*	H	1*e*
		5CO	10*e*	5CO	10*e*
			18*e*		18*e*
(ii)		Fe^{++}	6*e*	Fe	8*e*
		$2C_5H_5^-$	12*e*	$2C_5\dot{H}_5$	10*e*
			18*e*		18*e*

(iii)

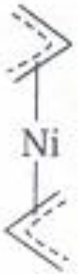


Cr	$6e$	Cr	$6e$
$2C_6H_6$	$12e$	$2C_6H_6$	$12e$
	$18e$		$18e$

(iv) $(OC)_5-Mn-Mn(CO)_5$

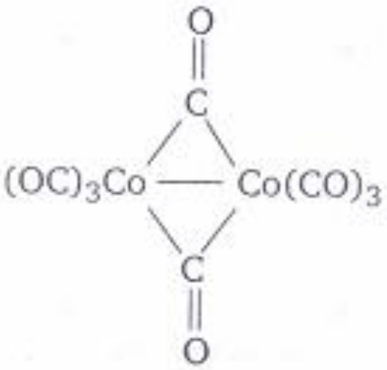
Mn	$7e$	Mn	$7e$
Mn—Mn	$1e$	Mn—Mn	$1e$
5CO	$10e$	5CO	$10e$
	$18e$		$18e$

(v)



Ni^{++}	$8e$	Ni	$10e$
$2C_3H_5^-$	$8e$	$2C_3\dot{H}_5$	$6e$
	$16e$		$16e$

(vi)



Co	$9e$	Co	$9e$
Co—Co	$1e$	Co—Co	$1e$
3CO	$6e$	3CO	$6e$
$2(\mu\text{-}CO)$	$2e$	$2(\mu\text{-}CO)$	$2e$
	$18e$		$18e$

(vii) $(OC)_5Mn—CH_3$

Mn^+	6*e*	Mn	7*e*
5CO	10*e*	5CO	10*e*
CH_3^-	2*e*	$\dot{C}H_3$	1*e*
	18*e*		18*e*

(viii) $[PtCl_4]^{\ominus\ominus}$

Pt^{++}	8*e*	Pt	10*e*
$4Cl^-$	8*e*	4Cl	4*e*
		Charge	2*e*
	16*e*		16*e*

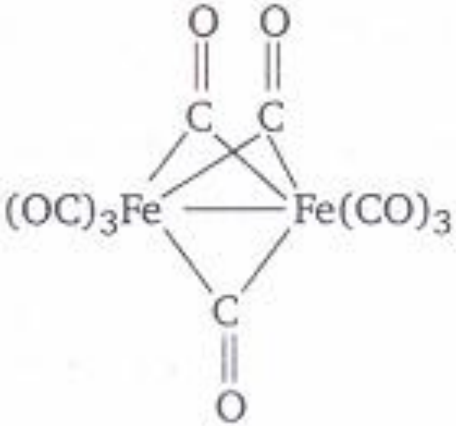
(ix) $[Cr(CO)_6]$

Cr	6*e*	Cr	6*e*
6CO	12*e*	6CO	12*e*
	18*e*		18*e*

(x) $[Fe(CO)_5]$

Fe	8*e*	Fe	8*e*
5CO	10*e*	5CO	10*e*
	18*e*		18*e*

(xi)



Fe	$8e$	Fe	$8e$
3CO	$6e$	3CO	$6e$
Fe—Fe	$1e$	Fe—Fe	$1e$
$3(\mu\text{-CO})$	$3e$	$3(\mu\text{-CO})$	$3e$
	$18e$		$18e$

(xii) $[Co(CO)_4]^\ominus$

Co	$9e$	Co	$9e$
4CO	$8e$	4CO	$8e$
Charge	$1e$	Charge	$1e$
	$18e$		$18e$

(xiii) $[Co(NH_3)_6]^{+++}$

Co	$9e$	Co	$9e$
$6NH_3$	$12e$	$6NH_3$	$12e$
Charge	$-3e$	Charge	$-3e$
	$18e$		$18e$

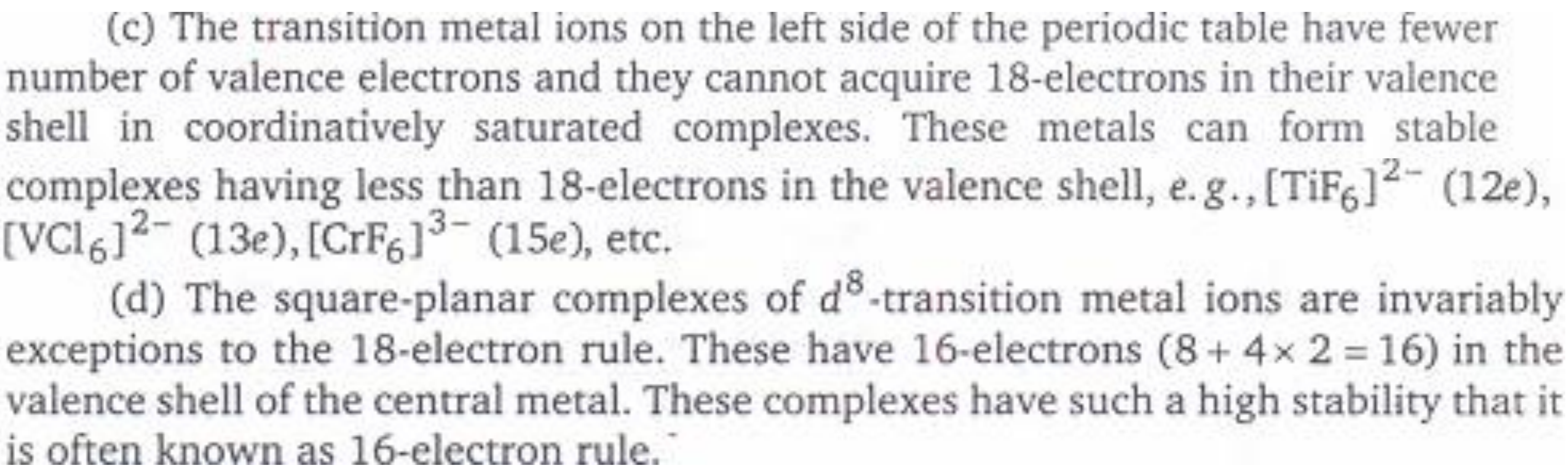
Limitations of the 18-Electron Rule

The 18-electron rule is not a hard and fast rule and it is not always strictly obeyed. There are a number of stable complexes in which the electron count is not equal to 18. It may be less than or greater than 18, viz., $H_3C—TiCl_3$ (8*e*), $(CH_3)_2NbCl_3$ (10*e*), $W(CH_3)_6$ (12*e*), $[Cr(H_2O)_6]^{++}$ (16*e*), $[Mn(H_2O)_6]^{++}$ (17*e*), $[V(CO)_6]$ (17*e*), $[Co(\eta^5-C_5H_5)_2]$ (19*e*), $[Ni(\eta^5-C_5H_5)_2]$ (20*e*), $[Zn(NH_3)_6]^{++}$ (22*e*), etc.

Most of the complexes which obey the 18-electron rule have strong π-acceptor ligands such as CO, $CH_2{=}CH_2$, CN^-, R_3P, etc., which stabilize the t_{2g} level by metal → ligand π bonding and increase the value of Δ_0. It makes the filling of highly antibonding e_g^* molecular orbitals energetically unfavourable. The splitting of 4*d* and 5*d* orbitals of second row and third row transition metals respectively in their complexes is more pronounced due to their larger size. It increases the value of Δ_0 and these metals are never found to have more than 18-electrons in their complexes with π-acceptor ligands. However, the 18-electron rule is generally not obeyed in the following cases :

(a) If the t_{2g} level is not stabilized through π-bonding by ligands, the t_{2g} level remains non-bonding and there may be less than 18-electrons in the valence shell of the central metal, *e.g.*, $[WCl_6]^{2-}$ (14*e*), $[TcF_6]^{2-}$ (15*e*), $[OsCl_6]^{2-}$ (16*e*), $[PtF_6]^{\ominus}$ (17*e*), etc.

(b) In the case of first row transition metal complexes, the value of Δ_0 is generally small and the weakly bonding e_g^* MOs can be filled without increasing the energy of the system much. Consequently, stable complexes with more than 18-electrons in the valence shell of central metal are well known, *e.g.*, $[Co(H_2O)_6]^{++}$ (19*e*), $[Ni(en)_3]^{++}$ (20*e*), $[Cu(NH_3)_6]^{++}$ (21*e*) and $[Zn(NH_3)_6]^{++}$ (22*e*).



(c) The transition metal ions on the left side of the periodic table have fewer number of valence electrons and they cannot acquire 18-electrons in their valence shell in coordinatively saturated complexes. These metals can form stable complexes having less than 18-electrons in the valence shell, *e.g.*, $[TiF_6]^{2-}$ (12*e*), $[VCl_6]^{2-}$ (13*e*), $[CrF_6]^{3-}$ (15*e*), etc.

(d) The square-planar complexes of d^8-transition metal ions are invariably exceptions to the 18-electron rule. These have 16-electrons $(8 + 4 \times 2 = 16)$ in the valence shell of the central metal. These complexes have such a high stability that it is often known as 16-electron rule.

Explanation : The splitting of d^8 atomic orbitals of a transition metal ion in square-planar crystal field is shown in fig. 1.3.

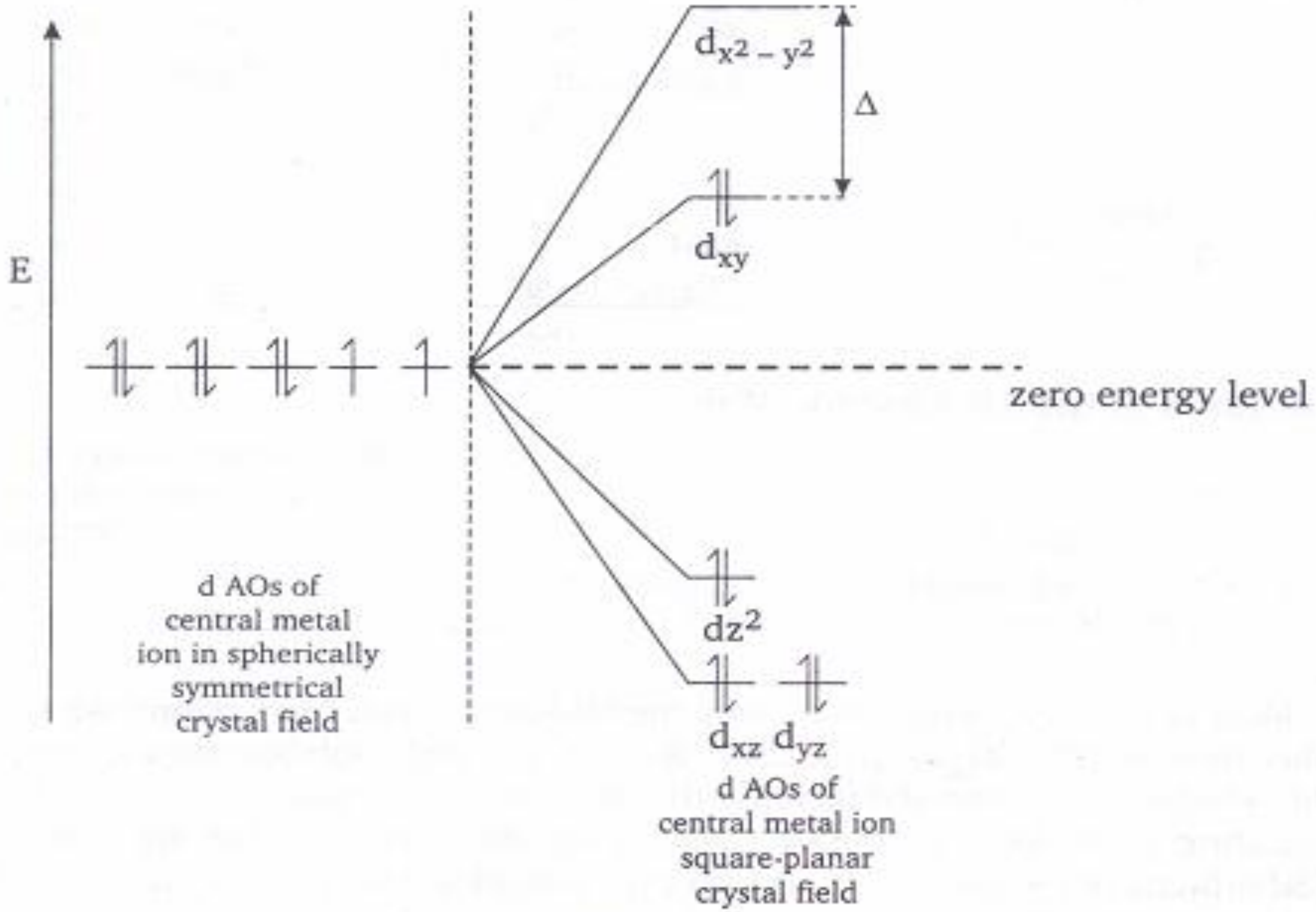


Fig. 1.3.

The energy difference between d_{xy} and $d_{x^2-y^2}$ atomic orbitals, *i.e.*, Δ is very large (even greater than Δ_0). Therefore, the accommodation of 9th electron of metal or electron-pair from incoming nucleophile in the $d_{x^2-y^2}$ orbital is energetically unfavourable. This is why the d^8 square-planar complexes of following transition metal ions are highly stable.