Organometallic Compounds

Definition: Compounds having at least one metal-carbon bond and the carbon moiety should belongs to the organic molecules.

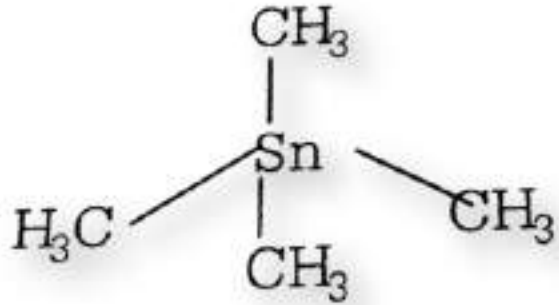
Important points:

- Depending on the type of *M-C* bond, molecules should be covalent, partially covalent, ionic, delocalized or localized in nature.
- Metal should belongs to the main group, transition or lanthanide or actinide atoms.
- Now a days, carbonyl, nitrosyl and cyanide complexes can also be considered as organometallic compounds.

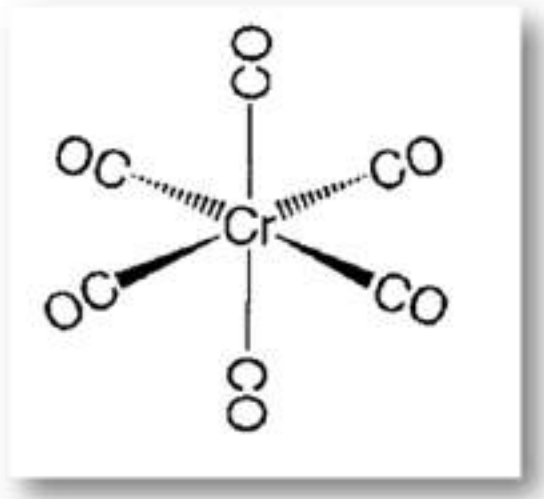
Classification of Organometallic Compounds

σ-bonded organometallic complexes: Formed mainly by the main group metal with 2c-2e bond.

E.g. CH_3MgBr, $Zn(C_2H_5)_2$, $Mg(CH_3)_2$

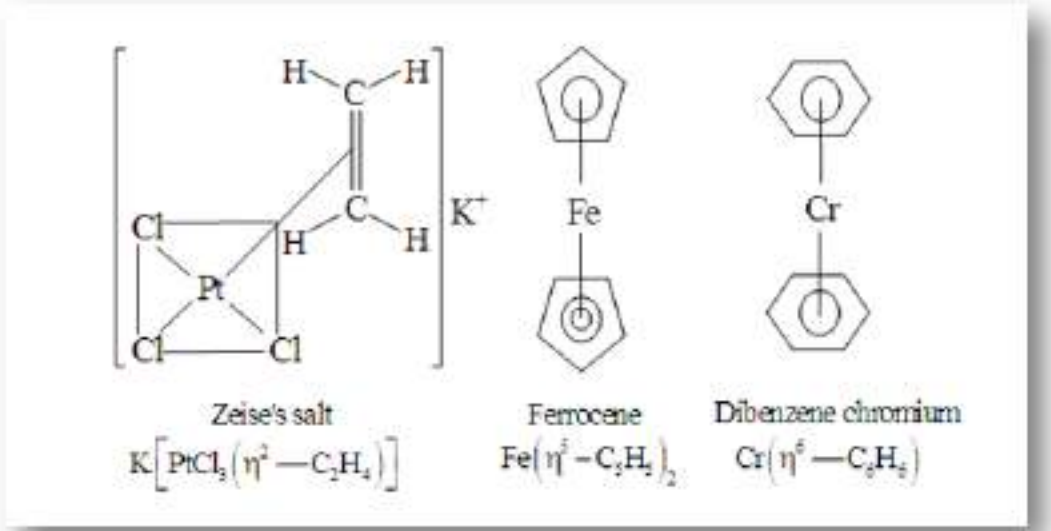


σ-donor, π-acceptor organometallic complexes: Involves the σ-donation of ligand followed by π-acceptance of the ligand. E.g. metal carbonyls, metal nitrosyls.

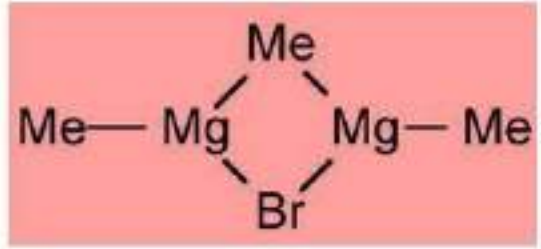


Π-donor, π-acceptor organometallic complexes: Involves π-donation of organic carbocyclic. Acyclic unsaturated ligand (alkene, benzene) from their respective bonding M.O followed by π-acceptance of the ligands.

Note: π-acceptor organometallic complexes are more stable than the σ-donor complexes.



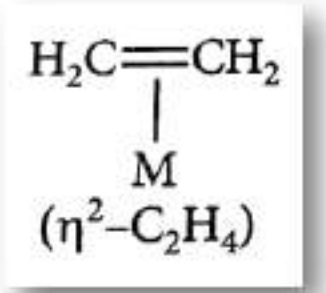
Non-classically bonded organometallic complexes: In this case the alkyl groups may act as the bridging groups between the metal centers. Instead of normal 2c-2e bond, electron deficient multicentered M-C bonds are formed. Eg. $Li_4(CH_3)_4$.

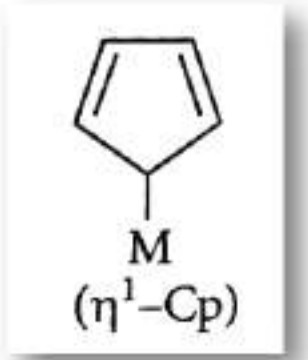


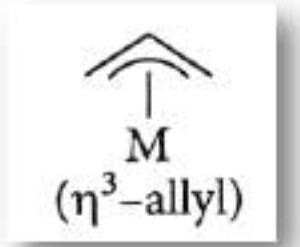
In this chapter we will mainly consider the transition metal organometallic complexes

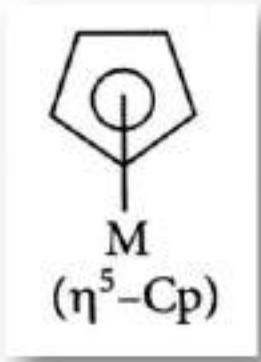
Heptacity of ligand: The number of carbon atom gets bound to the metal centers is expressed in terms of 'hap' to the nomenclature (η^x).

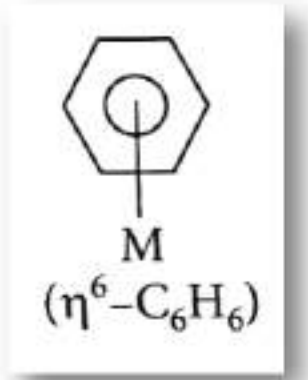
Examples:

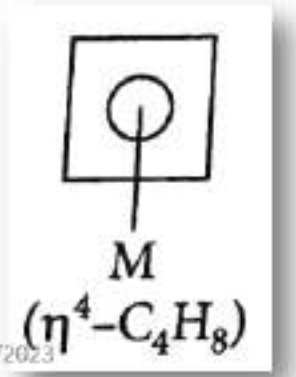


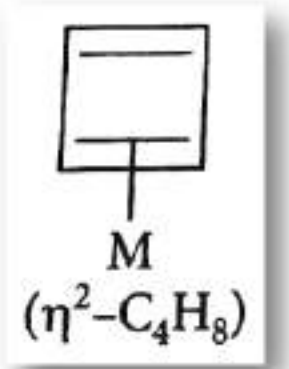


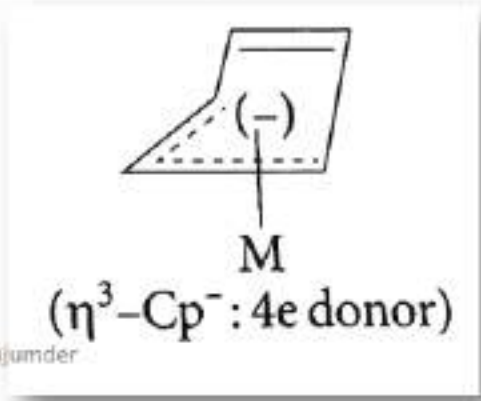












18-electron rule:

Thermodynamically stable organometallic complexes are formed when the sum of metal d-electrons and electrons donated by the ligands are equals to 18.

Note: Metals in low oxidation state and good π-acceptor ligands are favoured.

Ligands and their electron contributions:

There are two methods of calculating the contribution: one is neutral method and the rest one is oxidation state method.

Ligand	Neutral atom method	Oxidation state method		Ligand	Neutral atom method	Oxidation state method	
		Electron contribution	Formal charge			Electron contribution	Formal charge
Carbonyl (M–CO)	2	2	0	Halogen (M–X)	1	2	–1
Phosphine ($M–PR_3$)	2	2	0	Alkyl (M–R)	1	2	–1
Amine ($M–NR_3$)	2	2	0	Aryl (M–Ar)	1	2	–1
Amide ($M–NR_2$)	1	2	–1	Acyl [M–C(O)–R]	1	2	–1
Hydrogen (M–H)	1	2	–1	η^1-Cyclopentadienyl	1	2	–1
Alkene (sidewise) η^2-	2	2	0	η^1-Allyl	1	2	–1
Alkyne (sidewise) η^2-	2	2	0	η^3-Allyl	3	4	–1
η^2-C_{60}	2	2	0	η^5-Cyclopentadienyl	5	6	–1
Nitrosyl bent	1	2	–1	η^6-Benzene	6	6	0
Nitrosyl linear	3	2	+1	η^7-Cycloheptatrienyl	7	6	+1
Carbene ($M=CR_2$)	2	4	–2	Carbyne (M≡CR)	3	6	–3
Alkoxide (M–OR)	1	2	–1	Thiolate (M–SR)	1	2	–1
μ-CO [M–(CO)–M]	2	2	0	μ-H	1	2	–1
μ-Alkyne	4	4	0	μ-X (M–X–M) X = Halogen	3	4	–1
μ-Alkyl	1	2	–1	μ-Amido [M–(NR_2)–M]	3	4	–1
μ-Phosphido [M–(PR_2)–M]	3	4	–1	μ-Alkoxide [M–(OR)–M]	3	4	–1

Metal d-electrons counting:

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

Some examples of 18-electron rule:

$Cr(CO)_6$:

Cr(O) : 6e

6CO : $2 \times 6 = 12$

Total : 18 electron

$Cr(\eta^6\text{–}C_6H_6)_2$:

Cr(O) : 6e

$2(\eta^6\text{–}C_6H_6) : 2 \times 6 = 12$

Total : 18 electron

$[Fe(CO)_2(NO)_2]$ assuming NO^+ :

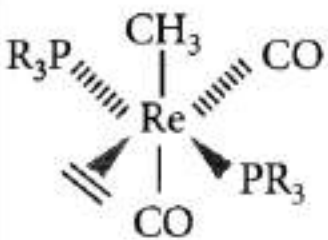
Fe : $8e^-$

$2 \times CO$: $2 \times 2 = 4e^-$

$2 \times NO$: $2 \times 3 = 6e^-$

Total : 18 electron

(calculation was done through neutral method)



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Re (+I) : d^6 ($6e^-$)

$2PR_3$: $4e^-$

$2CO$: $4e^-$

CH_3^- : $2e^-$

$H_2C = CH_2$: $2e^-$

Total : 18 electron

(Oxidation state method)

Or,

Re (O) : $7e^-$

$2PR_3$: $4e^-$

$2CO$: $4e^-$

CH_3 : $1e^-$

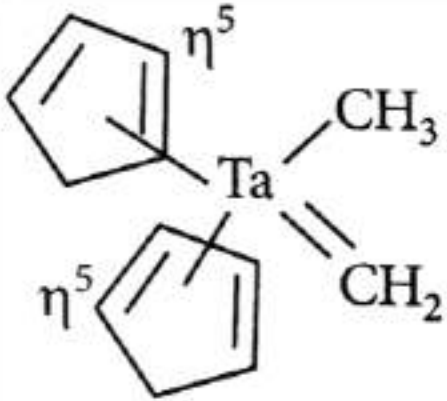
$H_2C = CH_2$: $2e^-$

Total : 18 electron

(Neutral method)

$Mn(CO)_4(\eta^3\text{–}C_3H_5)]$	:	Mn : – $7e^-$
		4CO : $2 \times 4 = 8e^-$
		$\eta^3\text{–}C_3H_5$: $3e^-$
		Total : 18 electron

$(\eta^5\text{–}C_5H_5)Fe(CO)_2Cl$	:	Fe(O) : $8e^-$
		$(\eta^5\text{–}C_5H_5)$: $5e^-$
		2CO (terminal) : $4e^-$
		Cl : $1e^-$
		Total : 18 electron



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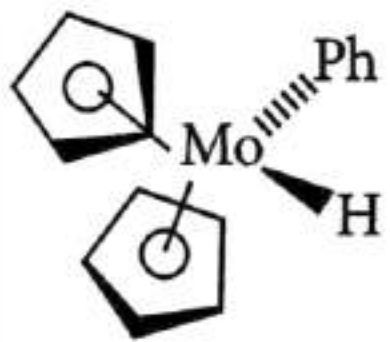
Ta(O)	: $5e^-$
$2(\eta^5\text{–}C_p)$	: $10e^-$
CH_3	: $1e^-$
Carbene	: $2e^-$
Total	: 18 electron



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Mo(O)	: $6e^-$
	: $5 \times 2 = 10e^-$
Ph	: $1e^-$
H	: $1e^-$
Total	: 18 electron

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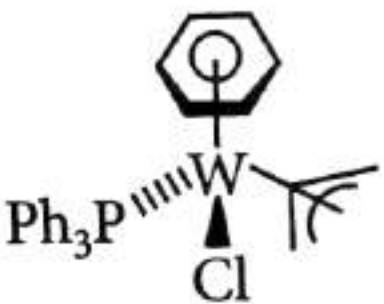
Rh : $9e^-$

 : $5e^-$

 : $4e^-$

Total : 18 electron



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W : $6e^-$

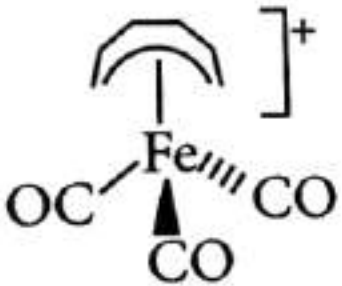
 : $6e^-$

Ph_3P : $2e^-$

Cl : $1e^-$

η^3–C_3H_5 : $3e^-$

Total : 18 electron

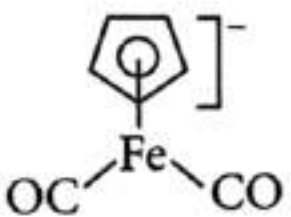


: Fe : $8e^-$

(η^5–pentadienyl) : $5e^-$

$3 \times CO : 3 \times 2 = 6e^-$

Total : 19 electron



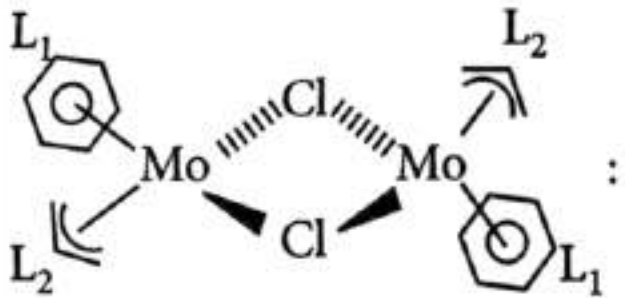
: Fe (O) : $8e^-$

η^5–C_p : $5e^-$

$2 \times CO : 2 \times 2 = 4e^-$

One negative charge : $1e^-$

Total : 18 electron



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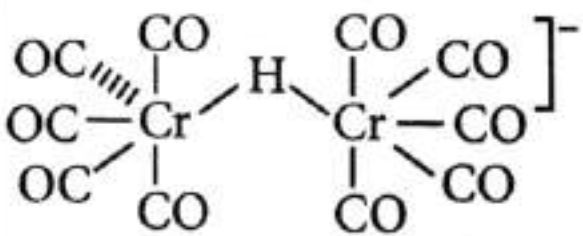
For each Mo—

Mo (I)	: $5e^-$
L_1	: $6e^-$
$2 \times Cl$	: $2 \times 2e^- = 4e^-$
L_2	: $3e^-$
Total	: 18 electron



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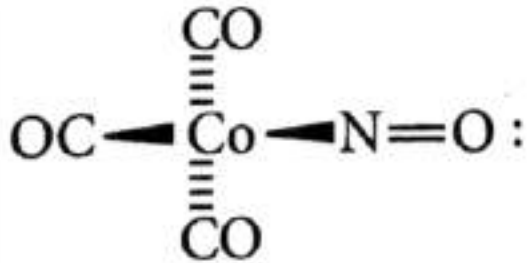
Cr (O)	: $6e^-$
$5 \times CO$	: $5 \times 2e^- = 10e^-$
H	: $1e^-$
Negative charge	: $1e^-$
Total	: 18 electron

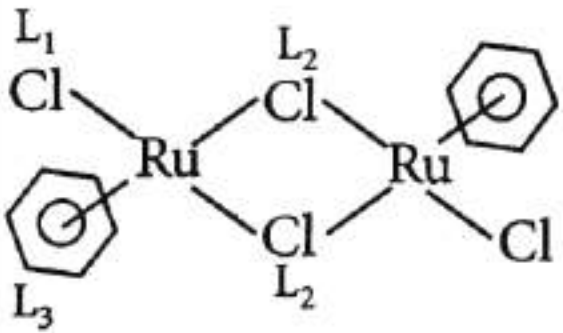


Co(O) : $9e^-$

$3 \times CO$: $3 \times 2e^- = 6e^-$

NO (linear) : $3e^-$

Total : 18 electron



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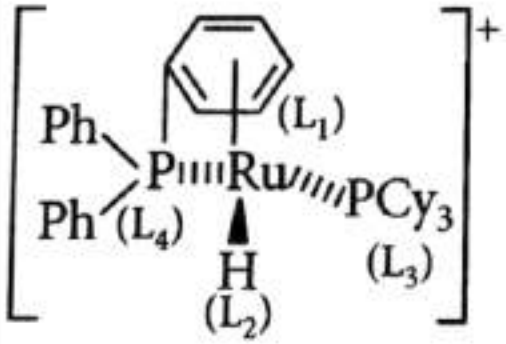
For each Ru (II) : $6e^-$

L_3 : $6e^-$

L_1 : $2e^-$

$2L_2$: $2 \times 2e^- = 4e^-$

Total : 18 electron



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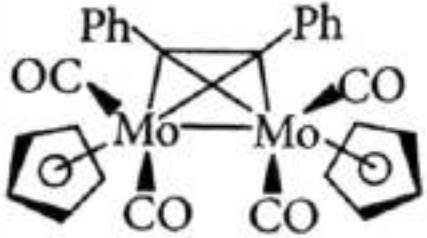
Ru (o)	: $8e^-$
L_1	: $6e^-$
L_2	: $1e^-$
L_3	: 2e
L_4	: 2e
Total	: 19 electron



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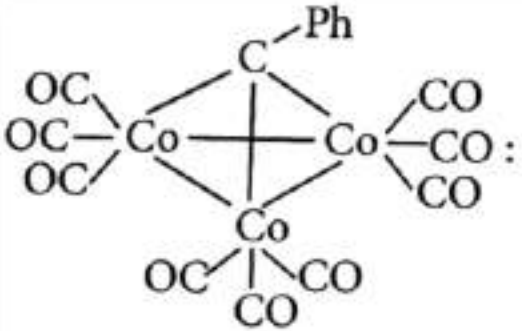
For each Mo(o)	: $6e^-$
2CO	: $2\times2 = 4e^-$
$(\eta^5\text{-}C_p)$	: $5e^-$
One Mo–Mo and two Mo–C bond	: $3e^-$
Total	: 18 electron



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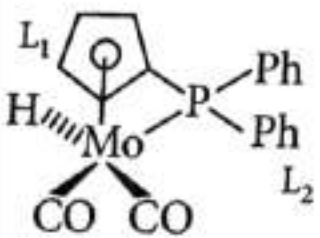
For each Co(O) : $9e^-$
3 CO : $3\times2e^- = 6e^-$
2Co–Co bond and 1Co–C bond : $3e^-$

Total : 18 electron



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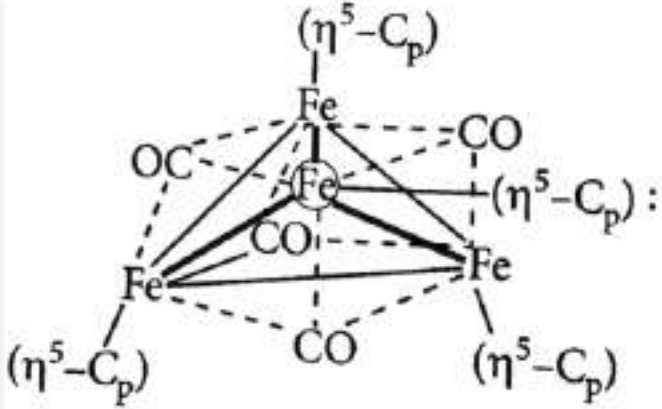
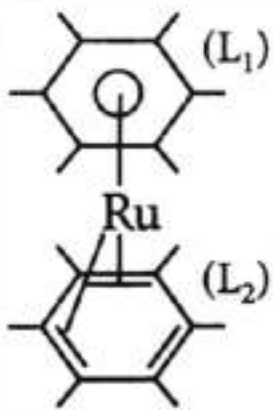
For each Mo(o) : $6e^-$
2CO : $2\times2e^- = 4e^-$
L_1 : $5e^-$
L_2 : $2e^-$
H : $1e^-$

Total : 18 electron



For each Fe(O) : $8e^-$
$(\eta^5\text{–}C_p)$: $5e^-$
3 Fe–Fe bond : $3e^-$
3 μ_3-binding mode of CO bond : $3\times\frac{2}{3} = 2e^-$

Total : 18 electron



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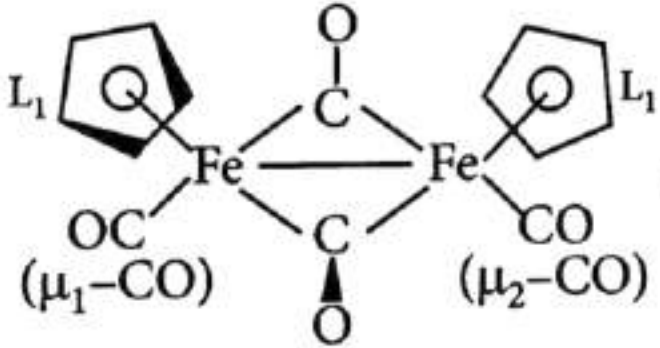
Ru(o) : $8e^-$
L_1 : $6e^-$
L_2 : $4e^-$

Total : 18 electron



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For each Fe (O)	: $8e^-$
L_1	: $5e^-$
μ_1CO	: $2e^-$
$2 \times \mu_2CO$	: $2e^-$
One Fe–Fe bond	: 1e
Total	: 18 electron