

# 过渡金属簇合物中 金属-金属键



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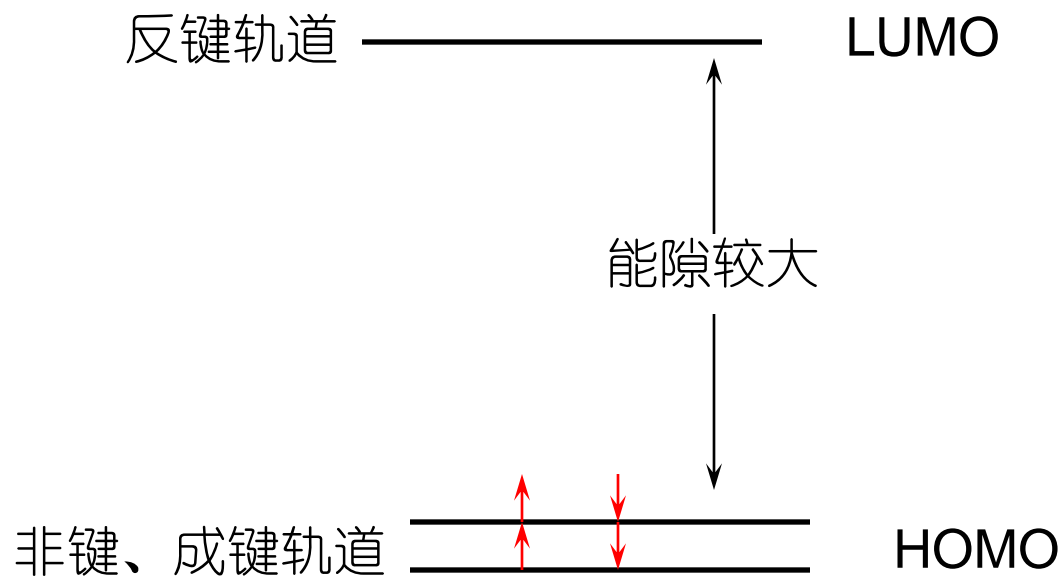
# 过渡金属簇合物中 金属—金属键

过渡金属簇合物是由3个或3个以上过渡金属原子直接成键，形成多面体或缺顶多面体的骨架，周围连接配体的化合物。

# 一、18电子规则和M-M键的键价

## 1. 18电子规则

在簇合物分子中，每个过渡金属原子倾向于在9个价轨道[5个(n-1)d, 1个ns, 3个np]中填满18个电子。即分子的全部成键分子轨道和非键轨道都填满电子，HOMO和LUMO间有较大能隙。



## 2. 簇合物中金属簇的键价及其计算

簇合物： $[M_nL_p]^q$

金属簇： $M_n$  即n个金属原子

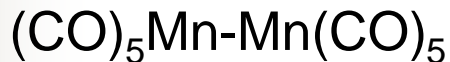
键价(b)：n个M原子间形成共价键的总数

二中心二电子键

$2c-2e$



补偿2个电子



$b=1$

三中心二电子键

$3c-2e$



补偿4个电子



$b=2$

键价  $b = (18n - g) / 2$

g包括：(1) n个M原子的价电子

(2) 配位体提供的价电子

(3) 簇合物的净电荷

# 配位体提供给分子骨干的电子数目 (骨干原子作不带净电荷计算)

配位体	配位形式	电子数目	配位体	配位形式	电子数目
H	$\mu_1, \mu_2, \mu_3$	1	NR <sub>3</sub> , PR <sub>3</sub>	$\mu_1$	2
B	int	3	NCR	$\mu_1$	2
CO	$\mu_1, \mu_2, \mu_3$	2	NO	$\mu_1, \mu_2, \mu_3$	3
CR	$\mu_3, \mu_4$	3	OR, SR	$\mu_1$	1
CR <sub>2</sub>	$\mu_1, \mu_2$	2	OR, SR	$\mu_2$	3
CR <sub>3</sub> , SiR <sub>3</sub>	$\mu_1, \mu_2$	1	O, S, Se, Te	$\mu_2$	2
$\eta^2$ -C <sub>2</sub> R <sub>2</sub>	$\mu_1$	2	O, S, Se, Te	$\mu_3$	4
$\eta^2$ -C <sub>2</sub> R <sub>4</sub>	$\mu_1$	2	O, S	int	6
$\eta^5$ -C <sub>5</sub> R <sub>5</sub>	$\mu_1$	5	F, Cl, Br, I	$\mu_1$	1
$\eta^6$ -C <sub>6</sub> R <sub>6</sub>	$\mu_1$	6	F, Cl, Br, I	$\mu_2$	3
C, Si	int	4	Cl, Br, I	$\mu_3, \mu_4$	5
N, P, As, Sb	int	5	PR	$\mu_3, \mu_4$	4

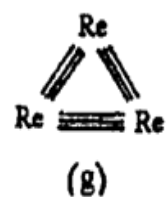
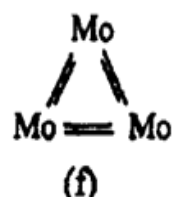
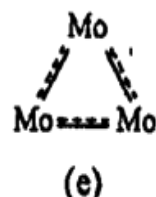
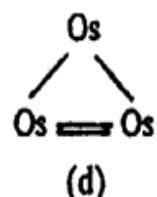
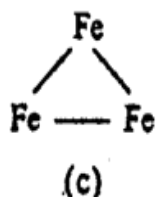
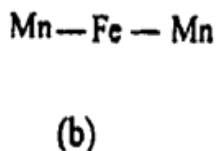
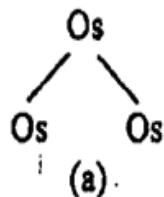
\*  $\mu_1$  = 端接配位体,  $\mu_2$  = 桥连 2 个原子配位体,  $\mu_3$  = 桥连 3 个原子配位体, int = 填隙原子。

## 二、键价和几何构型

### 1. 三核

一些三核过渡金属簇合物

簇合物	g	b	M—M /pm	M <sub>3</sub> 骨干的结构式
Os <sub>3</sub> (CO) <sub>9</sub> (μ <sub>3</sub> -S) <sub>2</sub>	50	2	Os—Os , 281.3	(a)
Mn <sub>2</sub> Fe(CO) <sub>14</sub>	50	2	Mn—Fe , 281.5	(b)
Fe <sub>3</sub> (CO) <sub>12</sub>	48	3	Fe—Fe , 281.5	(c)
Os <sub>3</sub> H <sub>2</sub> (CO) <sub>10</sub>	46	4	2Os—Os , 281.5 Os—Os , 268.0	(d)
[Mo <sub>3</sub> (μ <sub>3</sub> -S) <sub>2</sub> (μ <sub>2</sub> -Cl) <sub>3</sub> Cl <sub>6</sub> ] <sup>3-</sup>	44	5	Mo <sup>5/3</sup> —Mo , 261.7	(e)
[Mo <sub>3</sub> (μ <sub>3</sub> -O)(μ <sub>2</sub> -O) <sub>3</sub> F <sub>9</sub> ] <sup>5-</sup>	42	6	Mo—Mo , 250.2	(f)
Re <sub>3</sub> (μ <sub>2</sub> -Cl) <sub>3</sub> (CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>6</sub>	36	9	Re≡Re , 238.7	(g)





## 2. 四核

簇合物	g	b	M—M /pm	M <sub>4</sub> 骨干的 结构式
Re <sub>4</sub> (μ <sub>3</sub> -H) <sub>4</sub> (CO) <sub>12</sub>	56	8	6 个 Re <sup><math>\frac{1.33}{\text{---}}</math></sup> Re ,291	(a)
Ir <sub>4</sub> (CO) <sub>12</sub>	60	6	6 个 Ir—Ir ,268	(b)
Re <sub>4</sub> (CO) <sub>16</sub> <sup>2-</sup>	62	5	5 个 Re—Re ,299	(c)
Fe <sub>4</sub> (CO) <sub>13</sub> C	62	5	5 个 Fe—Fe ,263	(d)
Co <sub>4</sub> (CO) <sub>10</sub> (μ <sub>4</sub> -S) <sub>2</sub>	64	4	4 个 Co—Co ,254	(e)
Re <sub>4</sub> H <sub>4</sub> (CO) <sub>15</sub> <sup>2-</sup>	64	4	4 个 Re—Re ,302	(f)
Co <sub>4</sub> (μ <sub>4</sub> -Te) <sub>2</sub> (CO) <sub>11</sub>	66	3	3 个 Co—Co ,262	(g)
Co <sub>4</sub> (CO) <sub>4</sub> (μ-SEt) <sub>8</sub>	68	2	2 个 Co—Co ,250	(h)



(a)



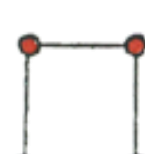
(b)



(c)



(d)



(e)



(f)

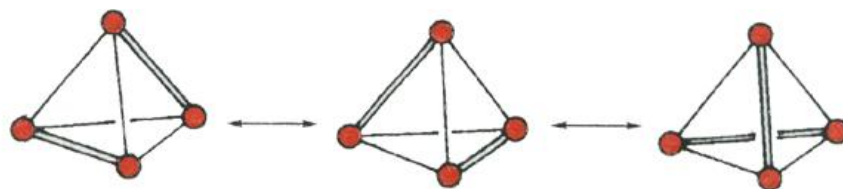


(g)



(h)

(a)

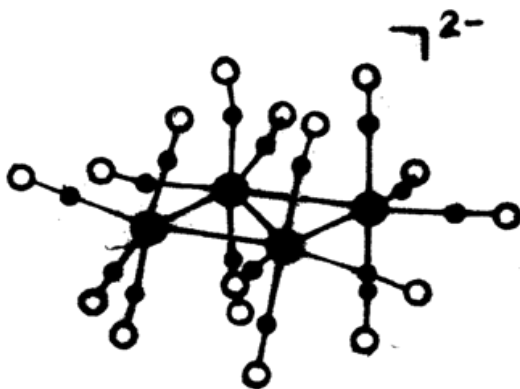


### 3种四核过渡金属簇合物的键价和结构



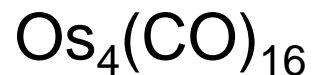
$$g=60$$

$$b=6$$



$$g=62$$

$$b=5$$



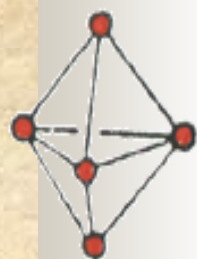
$$g=64$$

$$b=4$$



# 3. 五核

簇合物	$g$	$b$	棱边数目	图形
$\text{Os}_5(\text{CO})_{16}$	72	9	9	(a)
$\text{Fe}_5\text{C}(\text{CO})_{15}$	74	8	8	(b)
$\text{Os}_5\text{H}_2(\text{CO})_{16}$	74	8	8	(c)
$\text{Ru}_5\text{C}(\text{CO})_{15}\text{H}_2$	76	7	7	(d)
$\text{Ru}_5(\text{CO})_{14}(\text{NCCMe}_3)_2$	76	7	7	(e)
$\text{Os}_5(\text{CO})_{19}$	78	6	6	(f)
$\text{Re}_2\text{Os}_3\text{H}_2(\text{CO})_{20}$	80	5	5	(g)



(a)



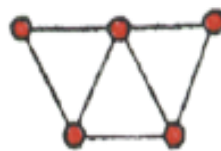
(b)



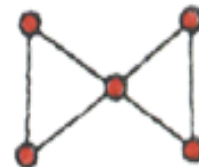
(c)



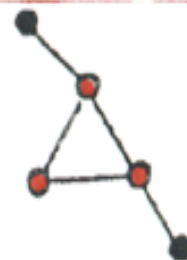
(d)



(e)



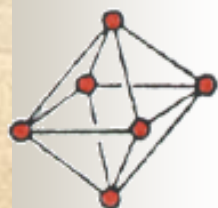
(f)



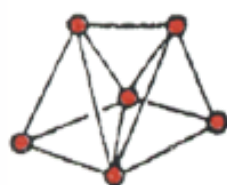
(g)

# 4. 六核

簇合物	$g$	$b$	棱边数目	图形
$\text{Mo}_6(\mu_3\text{-Cl})_8\text{Cl}_6^{2-}$	84	12	12	(a)
$\text{Nb}_6(\mu_2\text{-Cl})_{12}\text{Cl}_6^{4-}$	76	16	12	(a)
$\text{Rh}_6(\text{CO})_{16}$	86	11	12	(a)
$\text{Os}_6(\text{CO})_{18}$	84	12	12	(b)
$\text{Os}_6(\text{CO})_{18}\text{H}_2$	86	11	11	(c)
$\text{Os}_6\text{C}(\text{CO})_{16}(\text{MeC}\equiv\text{CMe})$	88	10	10	(d)
$\text{Rh}_6\text{C}(\text{CO})_{15}^-$	90	9	9	(e)
$\text{Os}_6(\text{CO})_{20}[\text{P}(\text{OMe})_3]$	90	9	9	(f)
$\text{Co}_6(\mu_2\text{-C}_2)(\mu_4\text{-S})(\text{CO})_{14}$	92	8	8	(g)



(a)



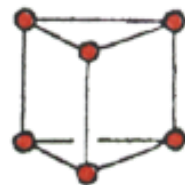
(b)



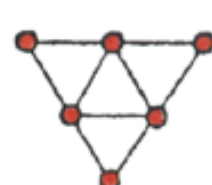
(c)



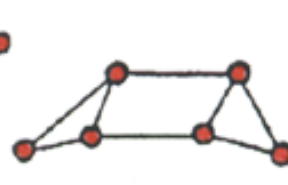
(d)



(e)

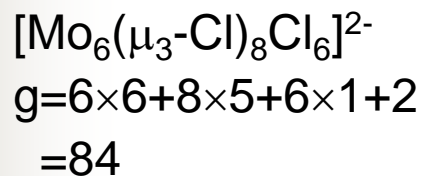
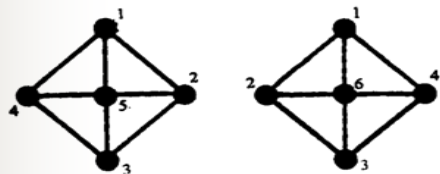
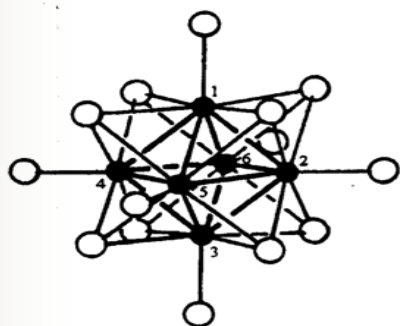


(f)

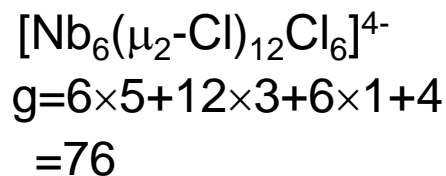
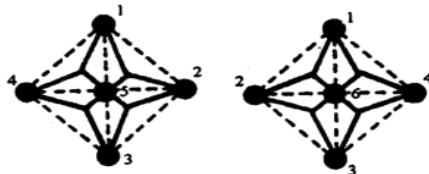
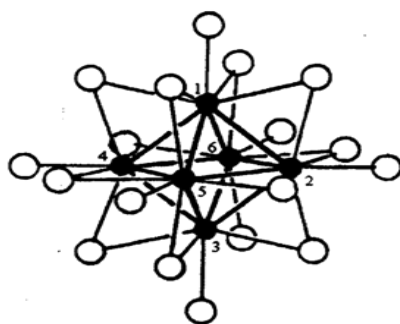


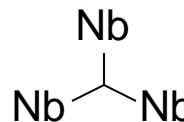
(g)

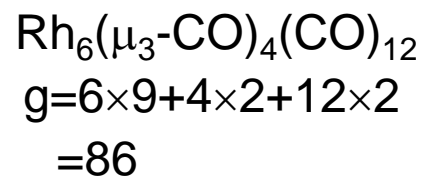
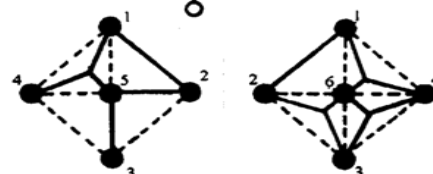
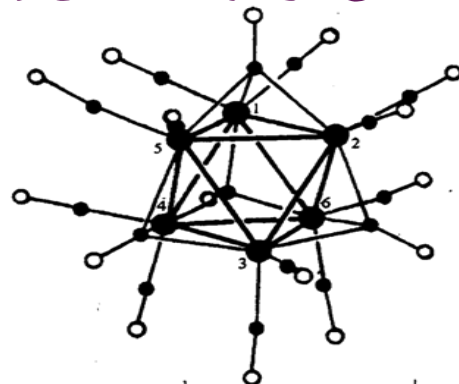
# 3种六核簇合物的结构和化学键

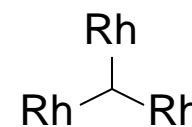


$b = 12$   
 12个2c-2e  
 Mo-Mo键



$b = 16$   
 8个3c-2e  
 键

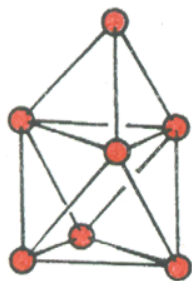


$b = 11$   
 3个2c-2e Rh-Rh键  
 4个3c-2e  
 键

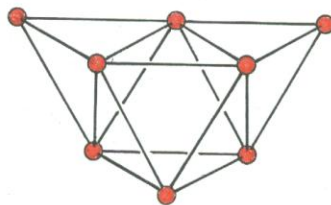
# 5. 六核以上

若干六核以上过渡金属簇合物

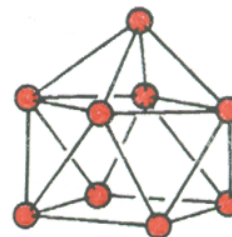
簇合物	<u>g</u>	<u>b</u>	结构(图16.4.1中的序号)	说 明
$\text{Os}_7(\text{CO})_{21}$	98	14	(a)	加帽八面体
$[\text{Os}_8(\text{CO})_{22}]^{2-}$	110	17	(b)	对位-双加帽八面体
$[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$	130	16	(c)	加帽四方反棱柱, 和 $\text{B}_9\text{H}_{13}$ 等键价
$[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{-}$	142	19	(d)	双加帽四方反棱柱, 和 $\text{B}_{10}\text{H}_{16}^-$ 等键价
$[\text{Rh}_{11}(\text{CO})_{23}]^{3-}$	148	25	(e)	3个共面八面体
$[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$	170	23	(f)	三角二十面体, 和 $\text{B}_{12}\text{H}_{12}^{2-}$ 等键价



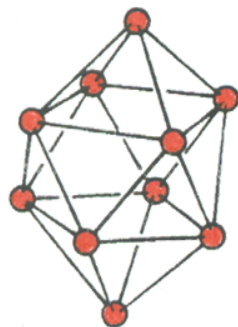
(a)



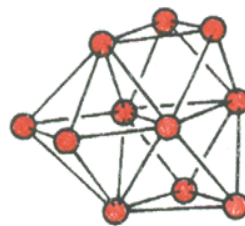
(b)



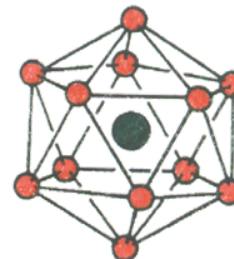
(c)



(d)



(e)



(f)



### 三、等同键价和等同结构

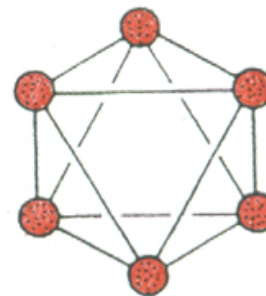
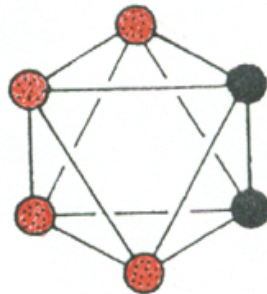
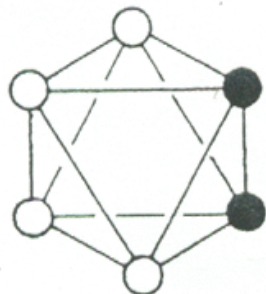
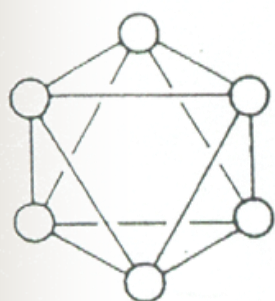
8电子规则（八隅律）：主族元素  
18电子规则：过渡金属元素 } 结合起来

含 $n_1$ 个过渡金属原子  
 $n_2$ 个主族元素原子 } 组成的簇合物骨干的键价

$$b = \frac{1}{2}(18n_1 + 8n_2 - g)$$



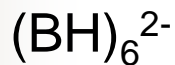
# 金属碳硼烷



○ (BH)

● (CH)

● Ru(CO)<sub>3</sub>

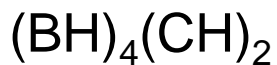


$g=26$

$b=11$

3个2c-2e 键

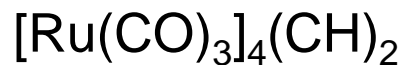
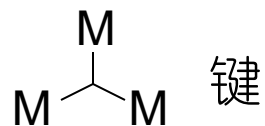
4个3c-2e 键



$g=26$

$b=11$

M—M 键



$g=66$

$b=11$

(M=B, C, Ru)



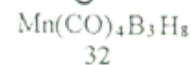
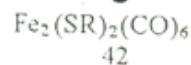
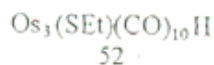
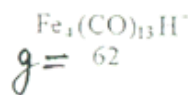
$g=86$

$b=11$

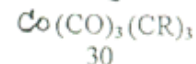
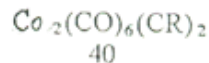
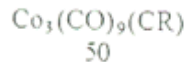
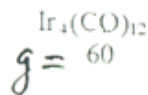
和 $\text{Rh}_6(\mu_3\text{-CO})_4(\text{CO})_{12}$ 相似

# 其他等同键价和等同结构系列举例

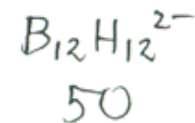
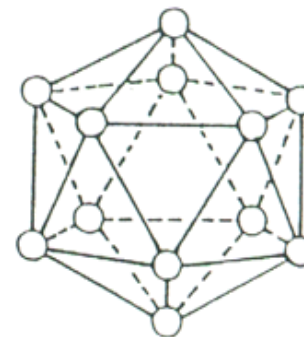
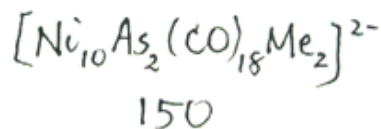
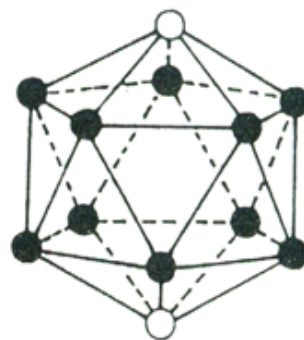
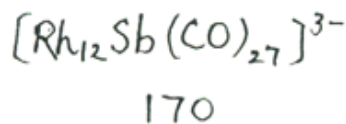
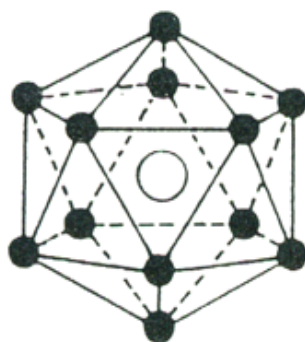
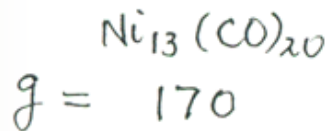
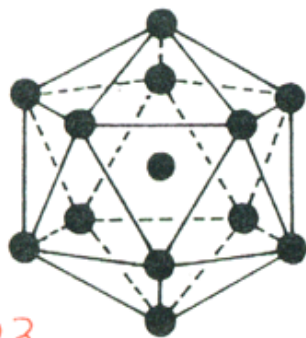
$b=5$



$b=6$



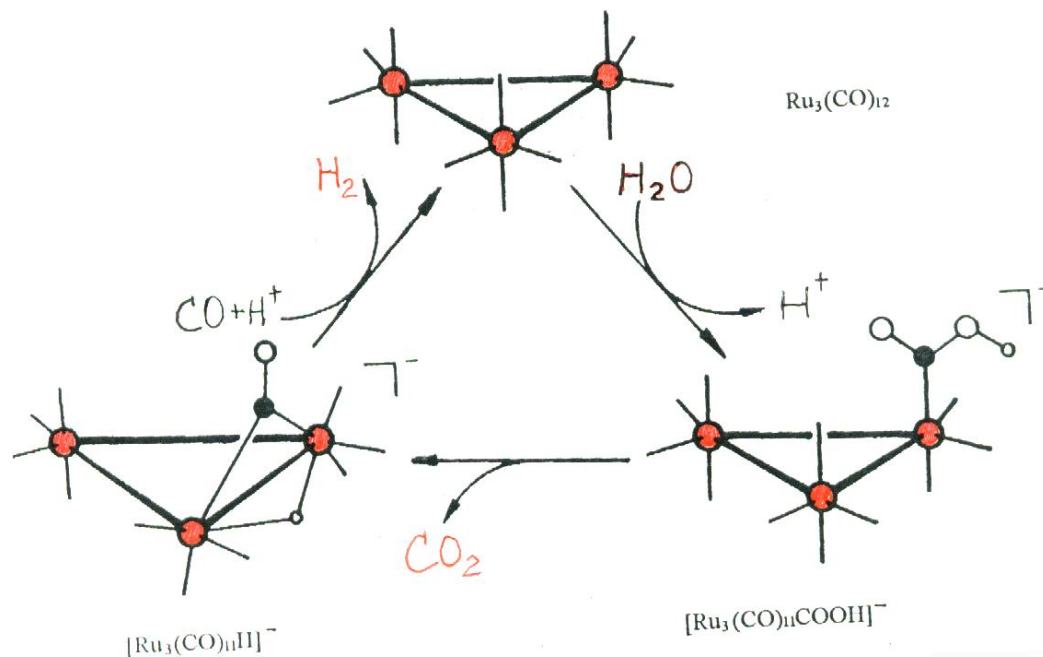
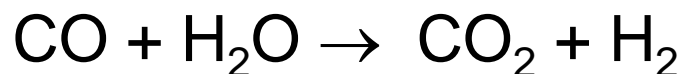
$b=23$



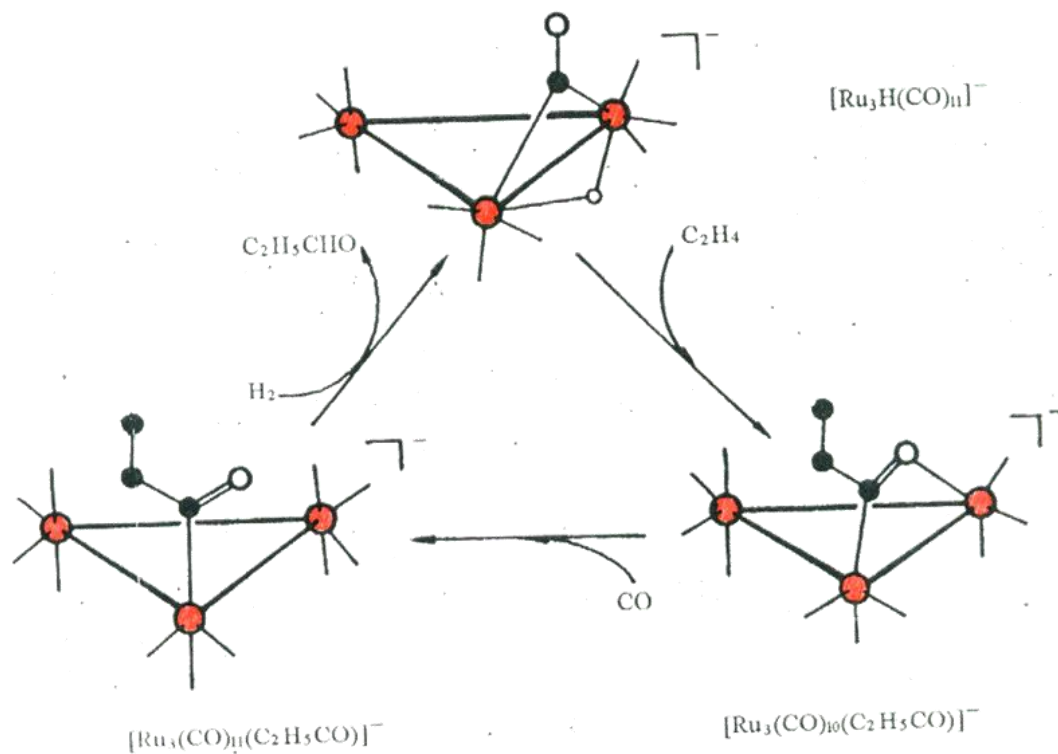
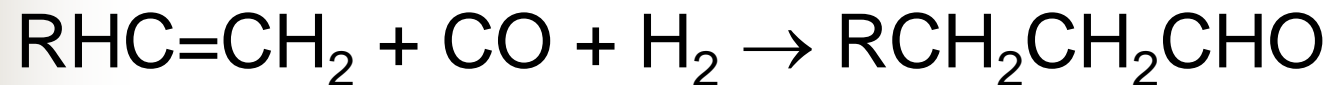
## 四、簇合物的催化功能

金属簇 ( $M_n$ ) 键价 ( $b$ ) 不变, 几何形状不变, 为反应物分子提供活动的舞台。具有不断接纳反应物放出产物的催化功能。

例1  $Ru_3(CO)_{12}$  催化水煤气反应

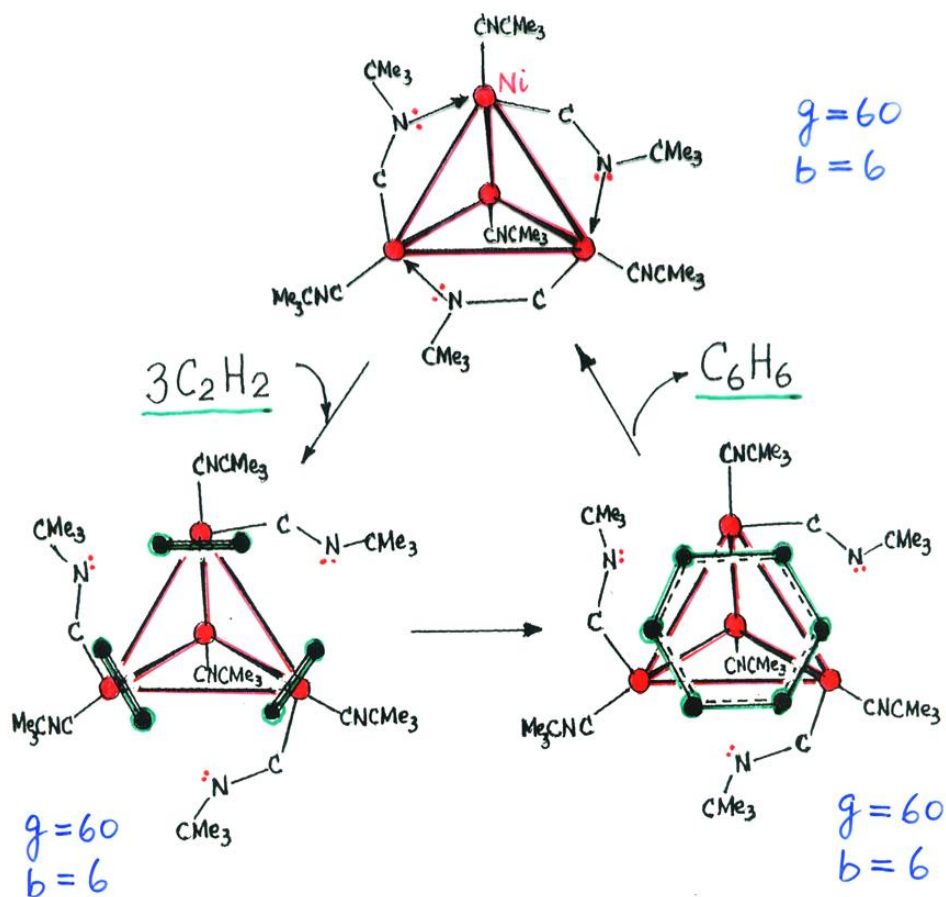
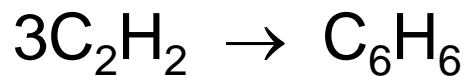


# 例2 $[\text{Ru}_3\text{H}(\text{CO})_{11}]^{-1}$ 催化羰基化反应





# 例3 $\text{Ni}_4(\text{CNCMe}_3)_7$ 催化乙炔合成苯

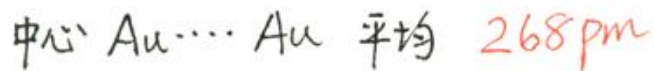
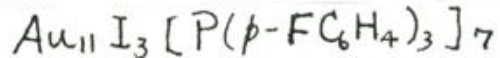
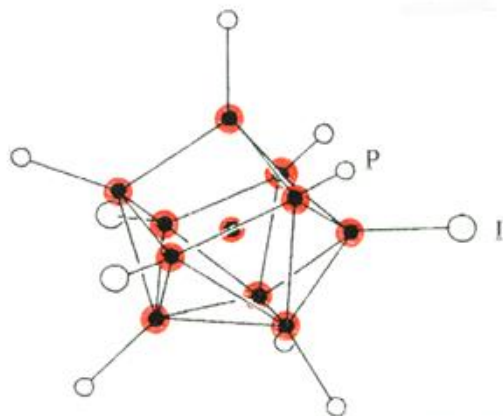
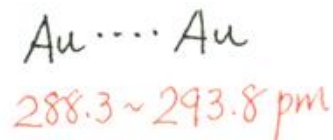
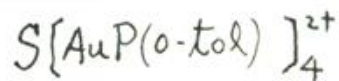
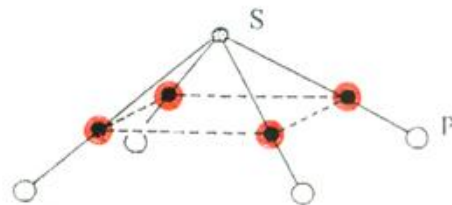
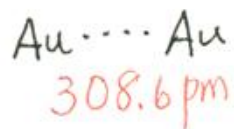
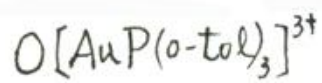
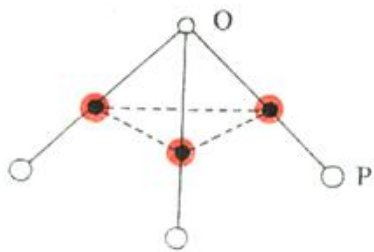




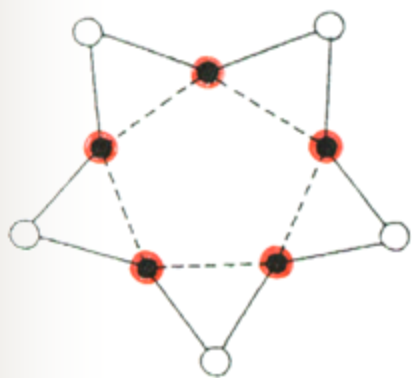
# 五、金属-金属相互作用

## 1. 亲金作用 (aurophilicity)

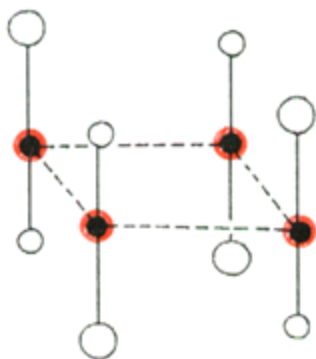
亲金作用指在一价金的簇合物分子中，非键的Au(I)原子间的相互吸引作用。



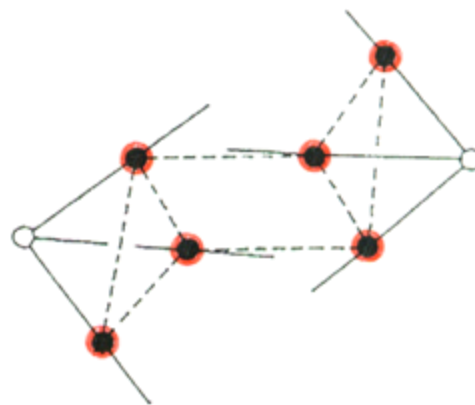
# 通过Au...Au相互吸引作用聚合



$Au_5(mes)_5$



$[AuClL]_4$

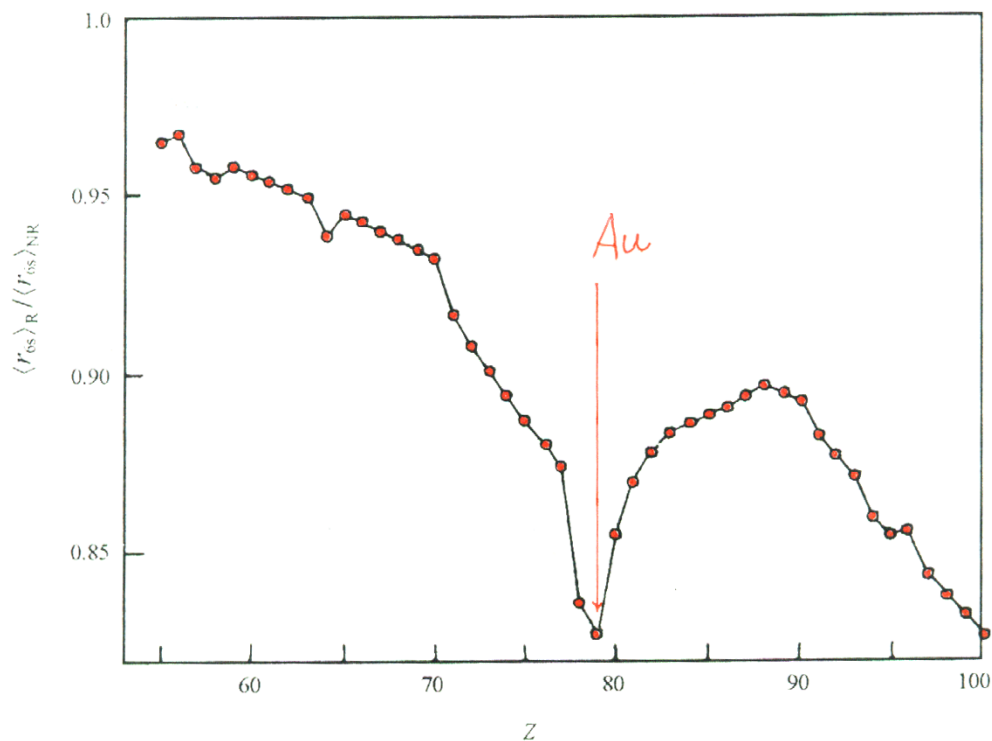


$[O(AuPPh_3)_3]_2$

一价金的电子组态为闭壳层结构Au(I):  $[\text{Xe}]4f^{14}5d^{10}6s^0$

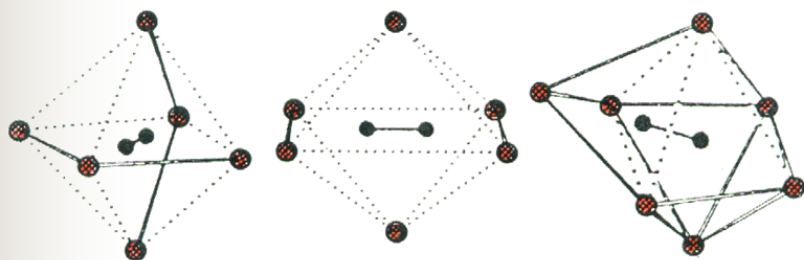
按常理，非键的同类原子应相互排斥，原子间距离大于范德华半径和： $2 \times 166\text{pm} = 332\text{pm}$

是什么原因导致亲金作用，使  $\text{Au}\cdots\text{Au}$  距离缩短？是相对论效应导致 **6s** 轨道收缩形成  $(6s5d)^{10}$  不呈现闭壳层结构



## 2. 亲银作用 (argentophilicity)

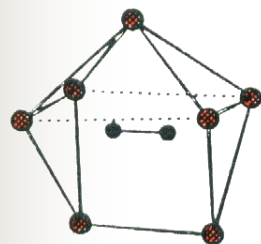
和亲金作用相似，在银簇合物和金银混合簇合物中呈现亲银作用。



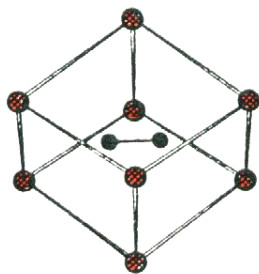
(a)  $[C_2@Ag_6]$

(b)  $[C_2@Ag_6]$

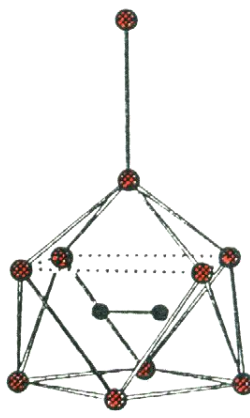
(c)  $[C_2@Ag_7]$



(d)  $[C_2@Ag_7]$



(e)  $[C_2@Ag_8]$



(f)  $[C_2@Ag_9]$

乙炔银复盐中包藏 $C_2^{2-}$ 的  
银多面体结构

(a)  $Ag_2C_2 \cdot 2AgClO_4 \cdot 2H_2O$

$Ag \cdots Ag$  (实线)

(b)  $Ag_2C_2 \cdot 2AgNO_3$

292.5pm

(c)  $Ag_2C_2 \cdot 5.5AgNO_3$

291~336pm

(d)  $Ag_2C_2 \cdot 5AgNO_3$

271~336pm

(e)  $Ag_2C_2 \cdot 6AgNO_3$

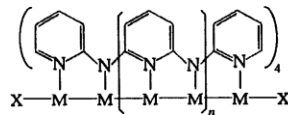
295~305pm

(f)  $Ag_2C_2 \cdot 8AgF$

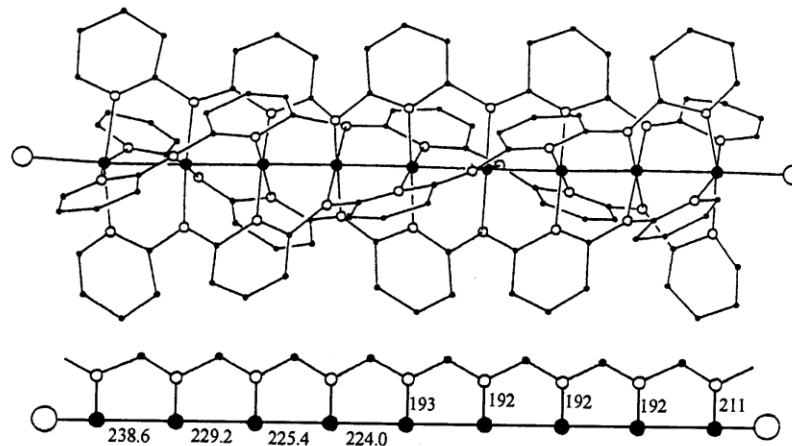


# 3. 金属线分子

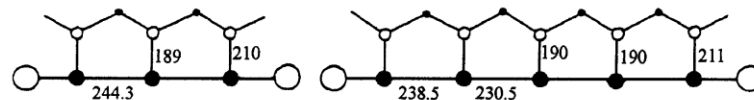
(a) 镍线



$n$	M(I)
0	Cr, Ru, Co, Rh, Ni, Cu
1	Cr, Co, Ni
2	Cr, Ni
3	Cr, Ni

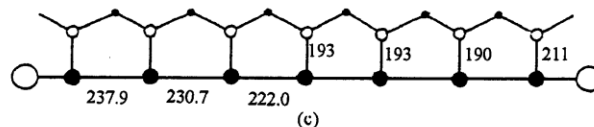


[Ni<sub>5</sub>(μ<sub>5</sub>-pep<sup>tea</sup>)<sub>4</sub>Cl<sub>2</sub>]分子的结构



(a)

(b)

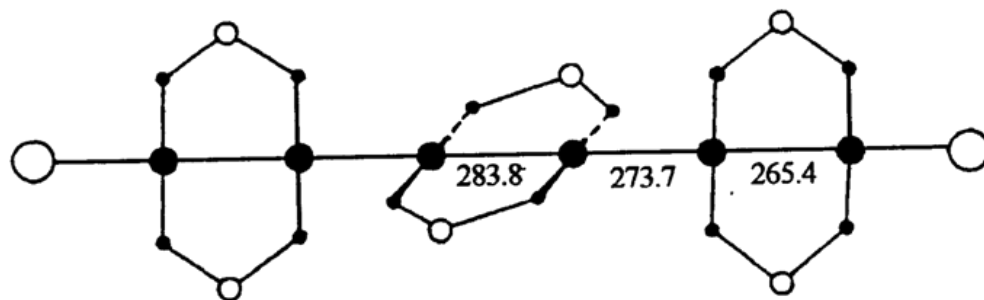
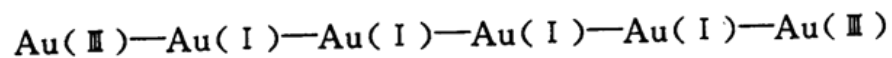
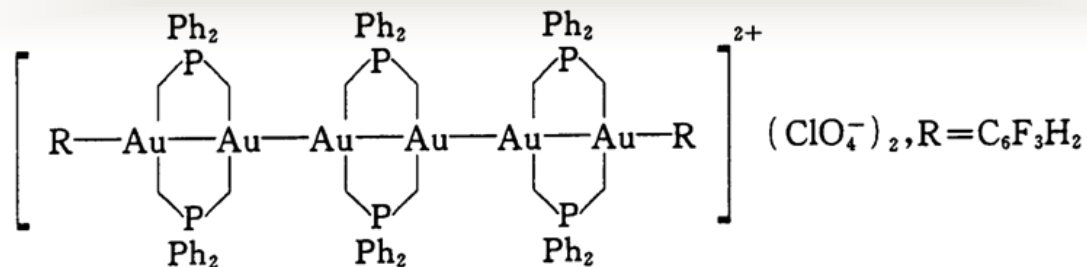


(c)

金属镍线性分子中 Ni-Ni 和 Ni-N 的键长, 单位为 pm



(b) 金线



(c) 铬线  $[\text{Cr}_5(\text{tpda})_4\text{Cl}_2] \cdot 2\text{Et}_2\text{O} \cdot 4\text{CHCl}_3$

