

FÉMORGANIKUS KÉMIA

(Előadási fóliamásolatok)

Szepes László

Szervetlen Kémiai Tanszék

2007-2008

Alapfogalmak és definíciók

A fémorganikus (FO) vegyületek *fém - szén* (M - C) kötést tartalmaznak; a fématom pozitív, a szénatom negatív polározottságú.

A szakirodalomban (bizonyos nagyvonalúsággal) *fémnek* tekintik azokat az elemeket, amelyek elektronegativitása kisebb, mint a szén elektronegativitása [$EN(M) < 2,5$].

A kötést kialakító C atom kémiai környezete:

- szerves ion, $Na^+ R^-$;
- szerves gyök, R_2Hg ;
- szerves molekula, Ar_2Cr .

Nem tekintjük FO vegyületeknek a *fém-karbonilokat*, *-cianidokat* és *-karbidokat*.

A FO vegyületek csoportosítása

I. Formai jegyek alapján

1) Tiszta (pure) FO vegyületek

ML_n (L=ligandum); L = R, H;

2) Vegyes (mixed) FO vegyületek

L = R, H, Hal, O, S stb.

A FO vegyületek csoportosítása (folyt.)

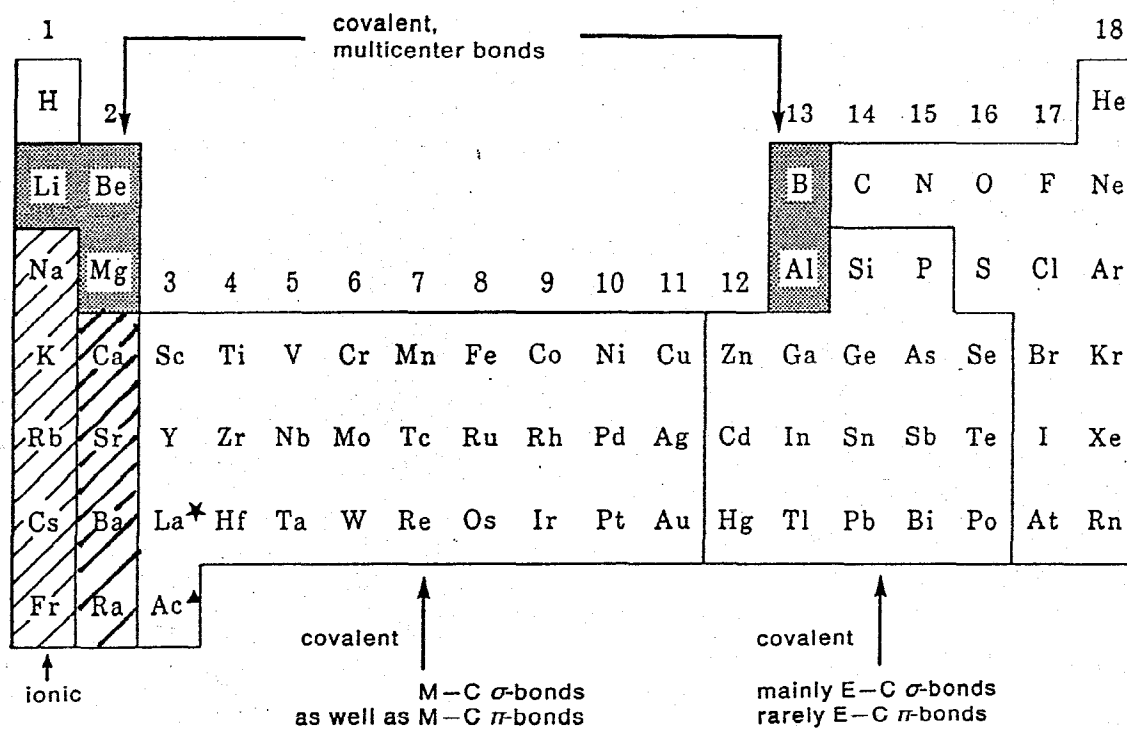
II. A fém-szén kötéstípus alapján

- 1) Ionos kötésű
- 2) Kovalens kötésű
- 3) Többcentrumú, elektronhiányos kötésű
- 4) π -komplexek
- 5) Egyebek
 - fém-szén többszörös kötésű
 - karboránok, stb.

III. A szerves ligandum donor-akceptor tulajdonsága alapján

- 1) σ -donor ligandumokkal alkotott vegyületek
 - a) anionos σ -donorokkal képzett vegyületek
fémalkilok, fémarilok;
 - b) semleges σ -donor és π -donor tulajdonságú ligandumokkal képzett vegyületek
- 2) π -donor ligandumokkal alkotott vegyületek

A periódusos rendszer elemeinek szerves származékai a fém-szén kötéstípus alapján



A FOK TÖRTÉNETÉNEK NÉHÁNY FONTOSABB ÁLLOMÁSA

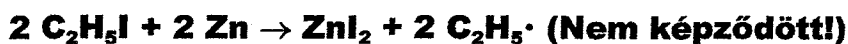
1760: Cadet – az első fo. vegyület



1827: Zeise – az első olefin-komplex



1849: Frankland – „etilgyök” előállítása (H₂ védőgáz!!!)



1868: Schützenberger – az első fémkarbonil



1871: Mendeleev, becslés a periódusos rendszer alapján

Ismert	Jósolt	Mért (1887)
Si(C₂H₅)₄	Eka- Si(C₂H₅)₄	Ge(C₂H₅)₄
	d = 0,96 g/cm³	d = 0,99 g/cm³
	fp = 160 °C	fp = 163,5 °C
Sn(C₂H₅)₄		

A FOK TÖRTÉNETÉNEK NÉHÁNY FONTOSABB ÁLLOMÁSA (2)

1900: Grignard

1943: Rochow – metil-klórszilánok → szilikonok

1951: Pauson és Miller – az első szendvics vegyület: Cp_2Fe

1955: Ziegler és Natta – poliolefinok előállítása



1964: Fischer – az első átmenetifém-karbén komplex



1965: Wilkinson, Coffey – alkének katalitikus hidrogénezése



1969: Timms – fématom-reaktor

1973: Fischer – az első átmenetifém-karbin komplex



A FOK TÖRTÉNETÉNEK NÉHÁNY FONTOSABB ÁLLOMÁSA (3)

1981: West



1983: Bergman, Graham

a C-H kötés aktiválása átmenetifém vegyületekkel

2005: Schrock, Grubbs, Chauvin – kémiai Nobel díj

metatézis alkalmazása szerves szintézisekben

A fémorganikus vegyületek szerepe az alap- és alkalmazott kutatásban; ipari termelés, néhány hétköznapi alkalmazás

- 1) Nagyobb rendszámú, főcsoportbeli elemek részvétele $p_{\pi} - p_{\pi}$ többszörös kötésekben;
- 2) Reaktív speciek stabilizálása fémkomplexekben;
- 3) Fématomot tartalmazó gyűrűk („metallaciklusok”);
- 4) Fémorganikus klaszterek;
- 5) Fémorganikus katalízis;
- 6) Szerves fémvegyületek mint modellek és prekursorok

Ipari termelés

- Szilikonok
- Pb-alkilek
- Szerves Al-vegyületek
- Szerves Sn-vegyületek
- Szerves Li-vegyületek

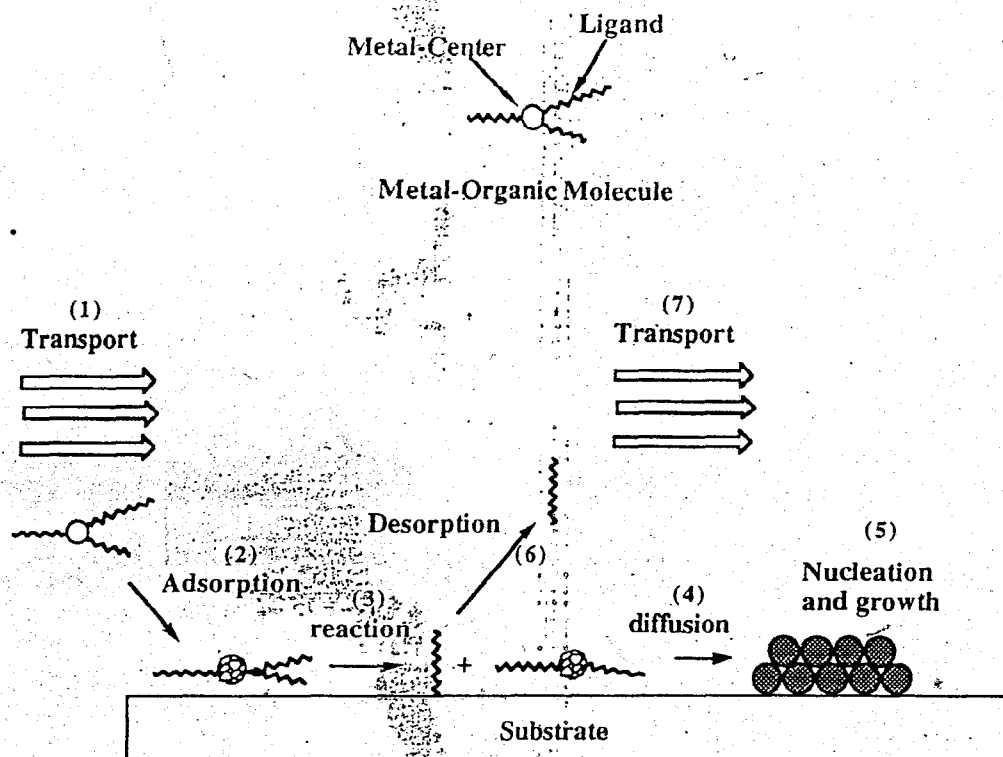


Figure 1-11. Illustration showing the fundamental steps involved in the CVD of a metal-organic molecule.

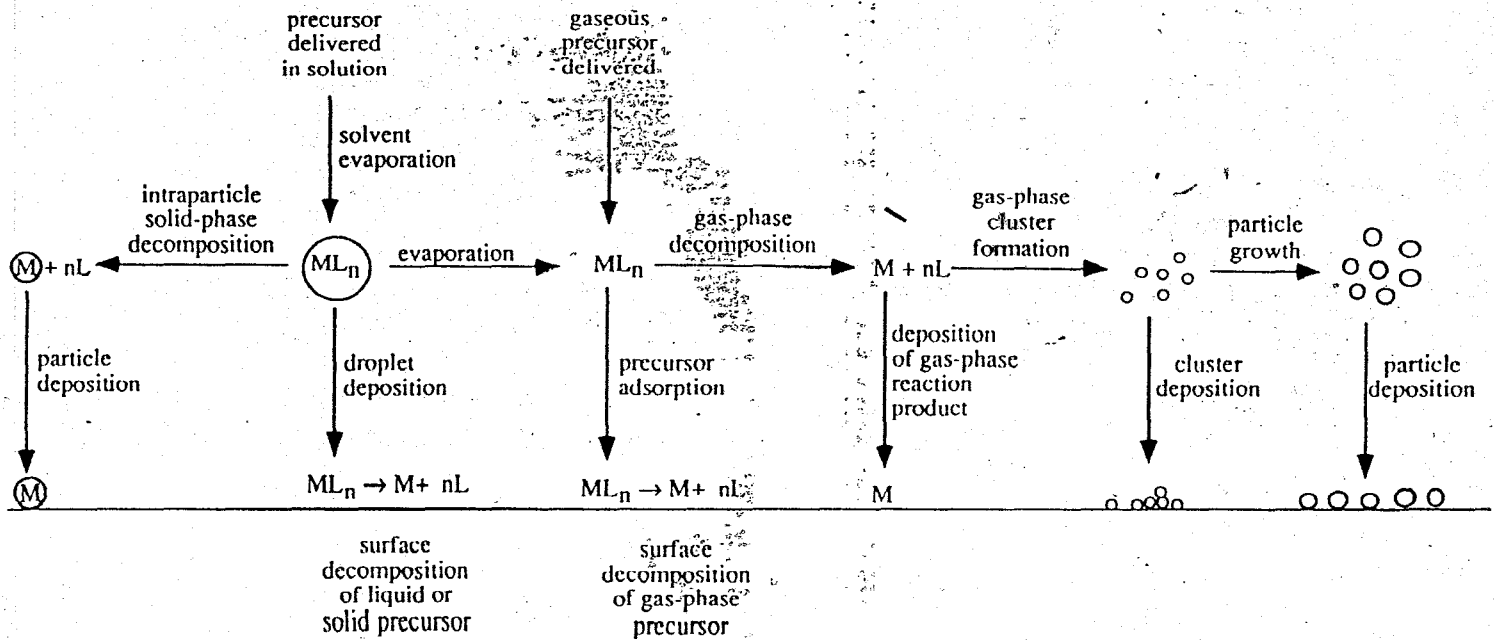


Figure 9-16 Schematic of overall reactor behavior (after Gurav et al. 103).

FOKI / 8.

A főcsoportbeli elemek szerves fémszármazékainak stabilitása

Kérdés: mivel szemben, milyen körülmények között?

Válasz: levegő (O₂), nedvesség (H₂O), hő (termikus stabilitás).

Egy fémorganikus vegyület reakciókészsége adott körülmények között függ:

a) termodinamikai tényezőktől ($\Delta G = \Delta H - T\Delta S$) \Rightarrow *stabilis, nem-stabilis;*

b) kinetikai tényezőktől (kis energiájú átmeneti komplex, üres d-pályák, E_{krit}) \Rightarrow *labilis, inert*

A főcsoportbeli elemek szerves vegyületeinek stabilitását kinetikai tényezők okozzák (a d-mező elemek σ -kötésű vegyületeinél fontos a β -elimináció kizárása)

Termokémiai adatok meghatározása /

(ΔH_f^0 , D, IE, AE)

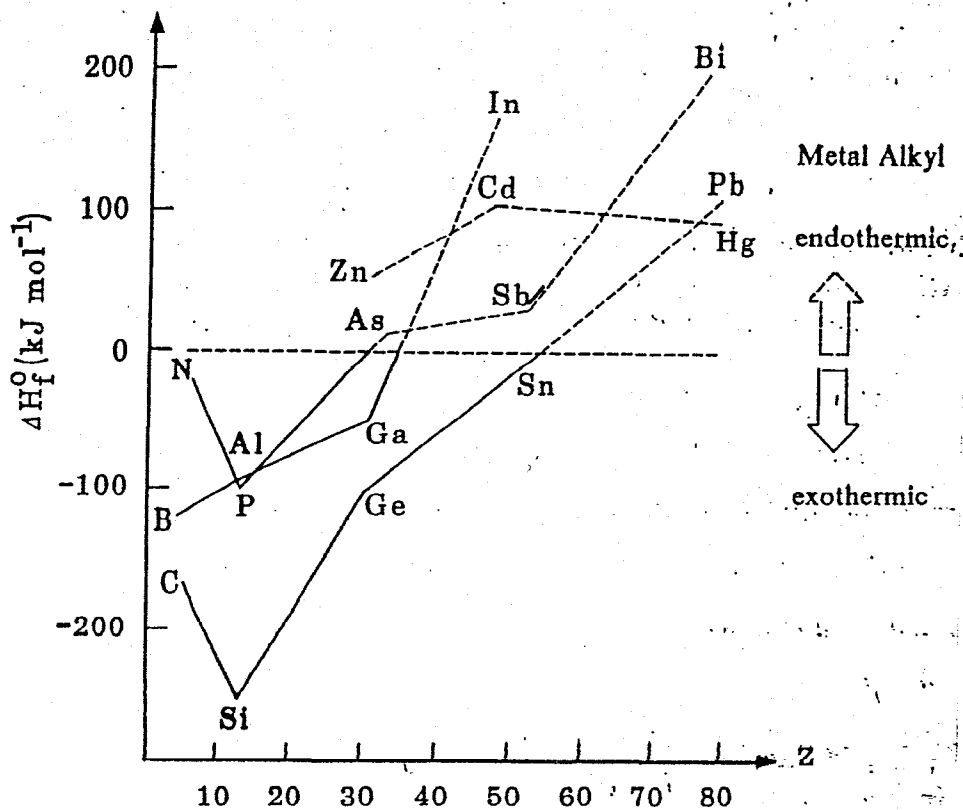
- 1) Kalorimetriásan, égéshők alapján;
- 2) Specifikus reakciók (hidrolízis, halogénezés, termikus bontás stb.) reakcióhőjének mérése alapján;
- 3) Gázfázisú ionkémiai (MS) mérések alapján;
- 4) Kvantumkémiai számolások segítségével.

Néhány szerves fémvegyület jellemző energetikai adata

Group 12			Group 13			Group 14			Group 15		
MMe ₂			MMe ₃			MMe ₄			MMe ₃		
M	ΔH_f°	\bar{E}	M	ΔH_f°	\bar{E}	M	ΔH_f°	E	M	ΔH_f°	\bar{E}
Zn	50	177	B	-123	365	C	-167	358	N	-24	314
Cd	106	139	Al	-81	274	Si	-245	311	P	-101	276
Hg	94	121	Ga	-42	247	Ge	-71	249	As	13	229
c.f.			In	173	160	Sn	-19	217	Sb	32	214
			Tl	—	—	Pb	136	152	Bi	194	141
			B-O		526	Si-O		452	As-O		301
			B-Cl		456	Si-Cl		381	Bi-Cl		274
			Al-O		500	Si-F		565			
			Al-Cl		420	Sn-Cl		323			

Data for M-C: *Comprehensive Organometallic Chemistry, 1* (1982) 5

Data for M-X: J. E. Huheey, *Inorganic Chemistry*, 3. Ed., A-32



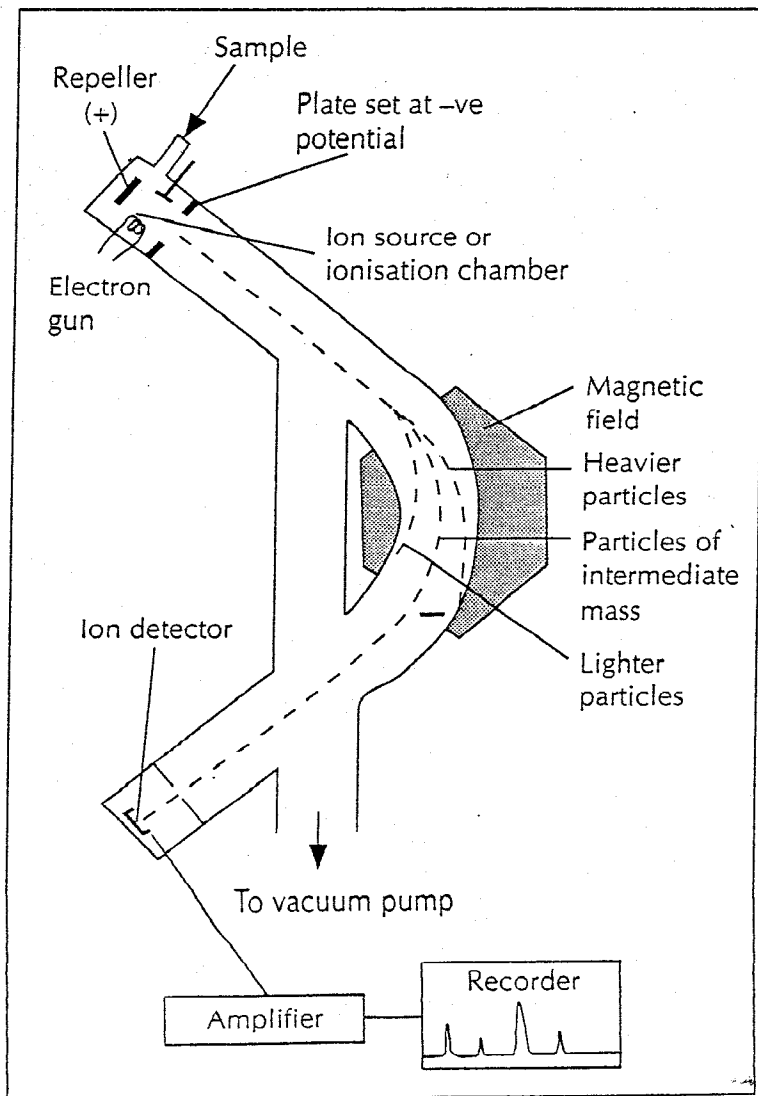
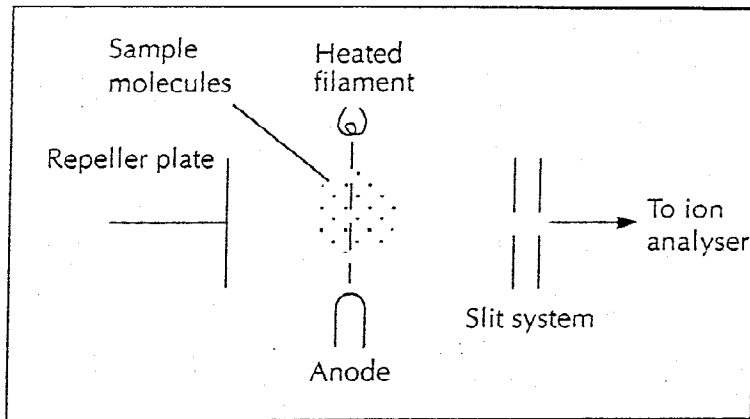
Néhány szerves fémvegyület tipikus viselkedése oxigénnel és vízzel szemben

Vegyület	ΔH_{comb}^0	Termodinamikai stabilitás	Kémiai tul.	Kinetikai viselkedés
Et_2Zn	-1920 kJ/mol	nem stabilis	piroforos	labilis
Me_4Sn	-3590 kJ/mol	nem stabilis	stabilis	inert

Vegyület	Viselkedés		A stabilitást/labilitást meghatározó tényezők
	levegőn	vízben	
Me_3In	piroforos	hidrolizál	- elektronhiány az In atomon - poláris In - C kötés
Me_4Sn	inert	inert	- árnyékolás az Sn atom körül - kis kötés-polaritás
Me_3Sb	piroforos	inert	- Sb magános el. pár

A reaktivitást meghatározó tényezők:

- magános elektronpár;
- kis energiájú üres MO;
- poláris fém-szén kötés.



FOKI/12.



usually easy to determine (Fig. 5). The two isotopes of chlorine have mass numbers of 35 and 37 respectively and they occur naturally in the ratio 76:24. Thus the appearance of two peaks differing by two mass units and in the approximate ratio 3:1 suggests the presence of a chlorine atom in the compound.

Some characteristic fragmentation patterns can be illustrated by using the example of two monosubstituted aromatic compounds - benzoic acid and methyl benzoate. For monosubstituted aromatics

a peak is expected at $m/z = 77$ corresponding to $C_6H_5^+$. This peak is often observed and it is present in the spectrum of both benzoic acid and methyl benzoate (Figs. 6a and b). However, bond breaking occurs more frequently one bond away from the benzene ring (see fragment at 105). Methyl benzoate and benzoic acid have similar fragmentation patterns and mass spectra. The compounds in this case can be identified from the mass of the molecular ion (136 for methyl benzoate and 122 for benzoic acid).

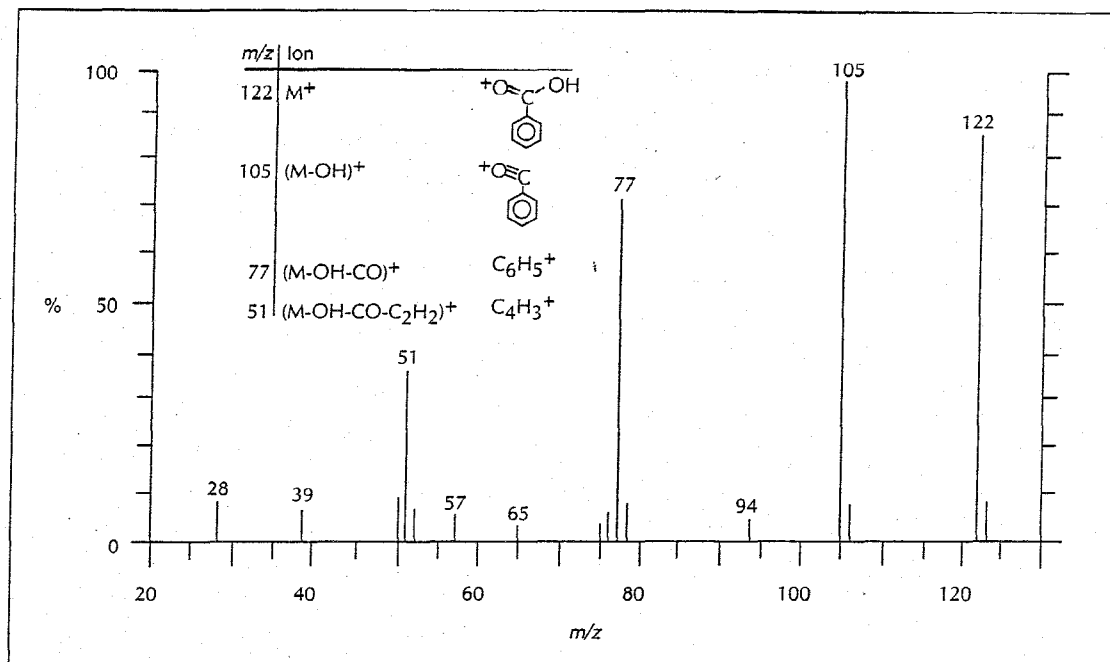


Figure 6a

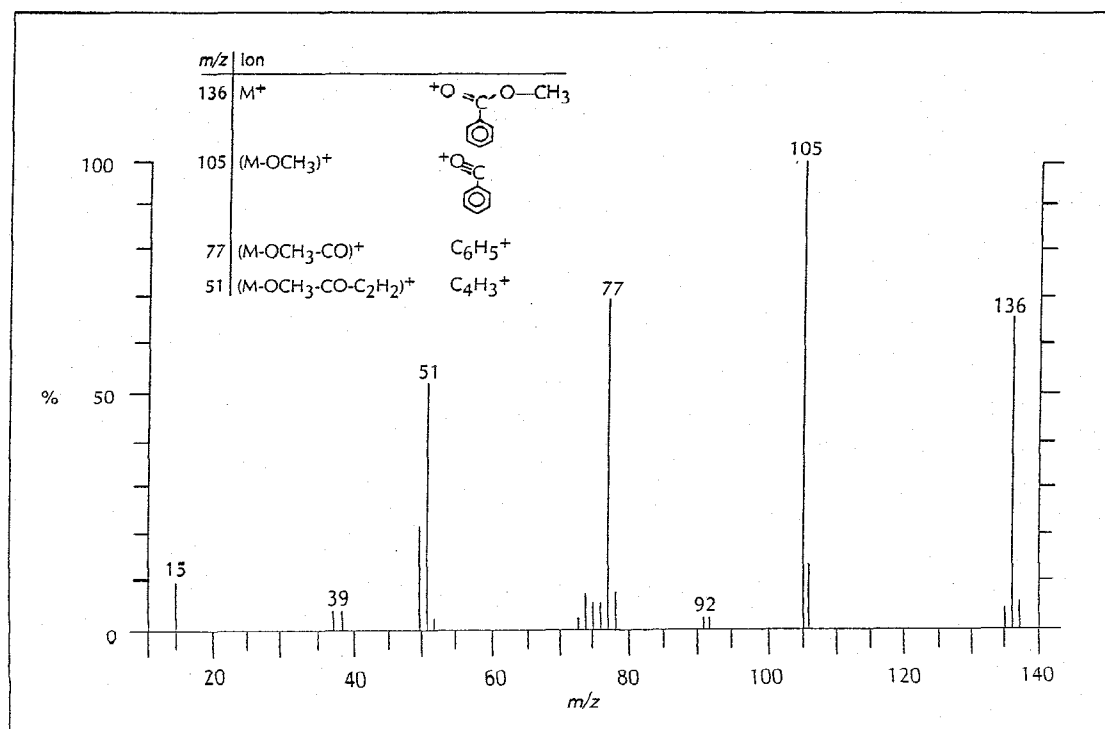
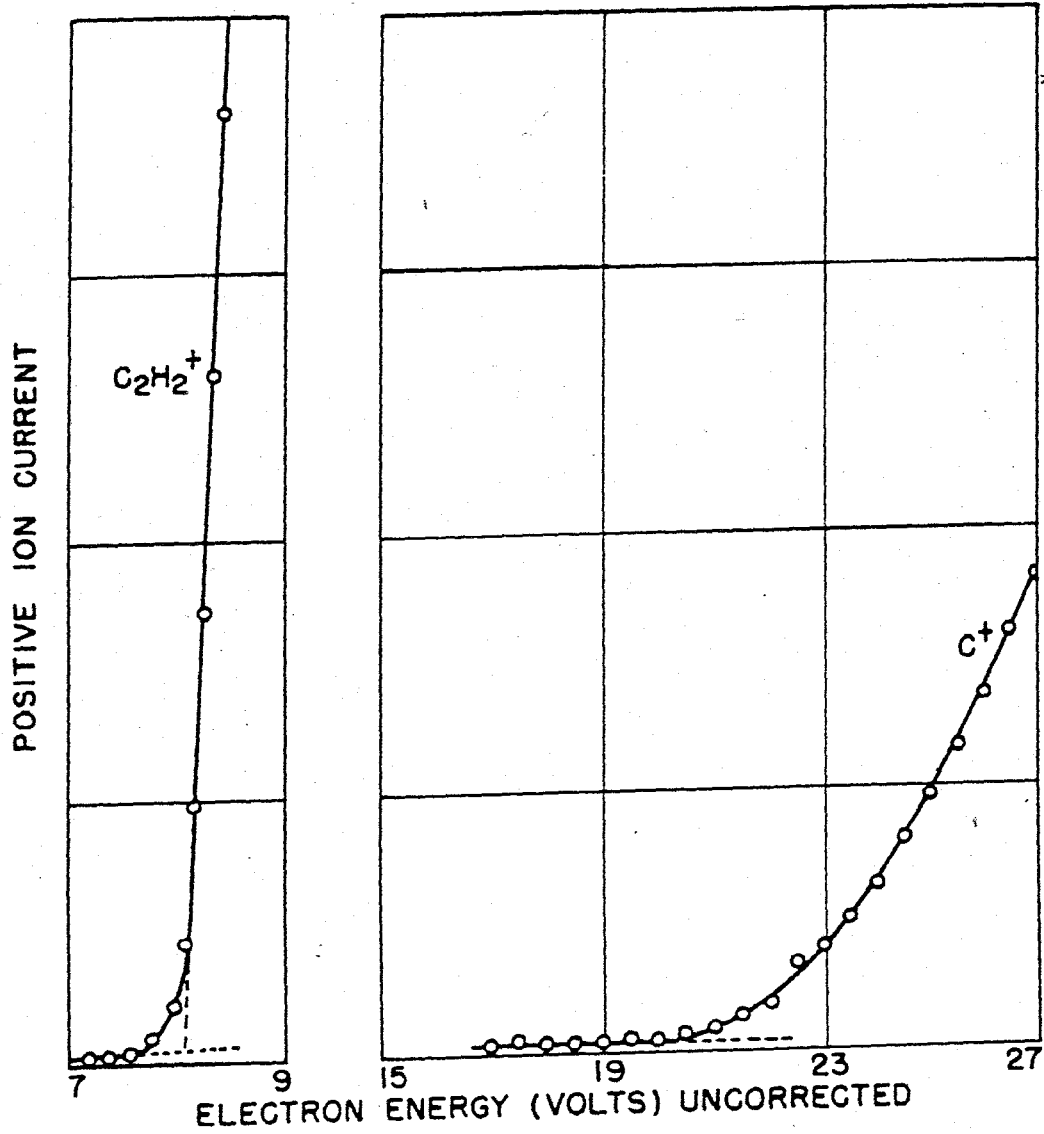


Figure 6b



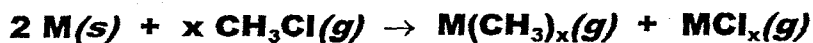
FOK I/14.

SZERVES σ -DONOROKKAL ALKOTOTT VEGYÜLETEK - SZINTÉZISEK

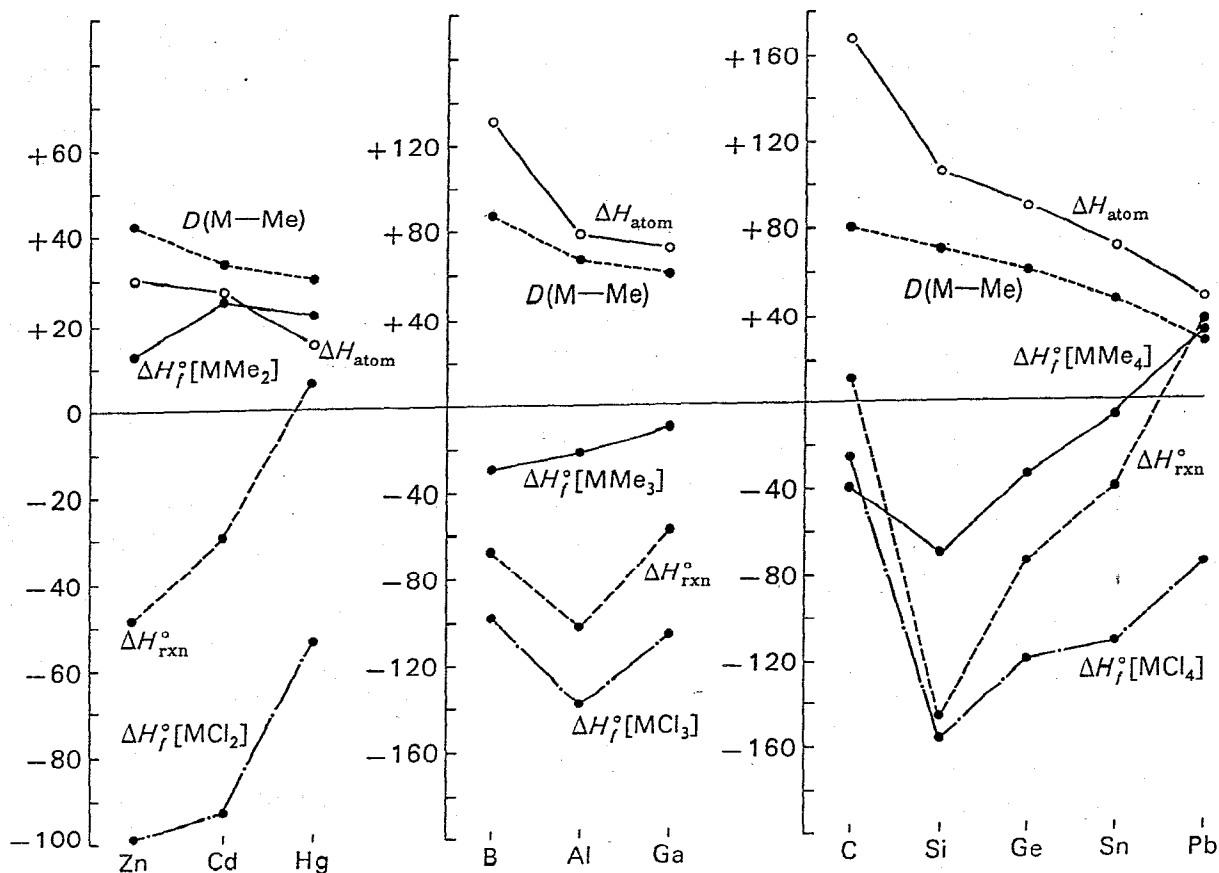
CARBON σ -DONORS - THE SYNTHESIS OF METAL ALKYL AND ARYLS

Közvetlen szintézis - Direct Synthesis

Termodinamikai megfontolások - Thermodynamic Considerations



M = Li; Mg; Zn, Cd, Hg; B, Al, Ga; Si, Ge, Sn, Pb

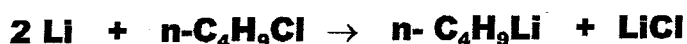


SZERVES σ -DONOROKKAL ALKOTOTT VEGYÜLETEK - SZINTÉZISEK

CARBON σ -DONORS-THE SYNTHESIS OF METAL ALKYL AND ARYLS

1) Közvetlen szintézis - *Direct Synthesis*

a) Alkil-lítium vegyületek - *Alkyl lithium compounds*

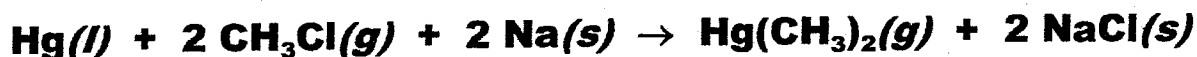
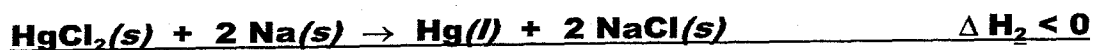


b) Nátrium-alkil és -aril vegyületek - *Sodium alkyls and aryls*



c) Magnézium-alkil és -aril vegyületek - *Alkyl- and arylmagnesium halides (Grignard reagents)*

d) Szerves higanyvegyületek - *Organic derivatives of mercury*



SZERVES σ -DONOROKKAL ALKOTOTT VEGYÜLETEK – SZINTÉZISEK

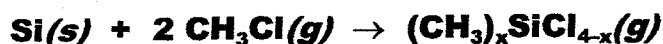
CARBON σ -DONORS–THE SYNTHESIS OF METAL ALKYL AND ARYLS

1) Közvetlen szintézis (folyt.)– *Direct Synthesis (cont.)*

e) Alumíniumorganikus vegyületek – *Alkylaluminum sesquihalides*



f) 14. csoport elemek: Si (Ge, Sn) + RX – *Grup 14 elements + RX*



...



Pb/Na ötvözet!!!

Pb/Na alloy!!!

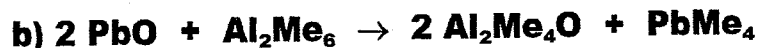
g) Átmenetifémek + RX → „fématom reaktor” (CC)

Transition metals + RX → „metal atom reactor” → co-condensation (CC)

2) Fémhalogenidek és -oxidok reakciója anionos alkilezőszerekkel

Reactions of Anionic Alkylating Agents with Metal Halides and Oxides

LiR, NaR, RMgX AlR₃

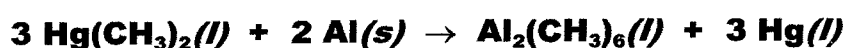


SZERVES σ -DONOROKKAL ALKOTOTT VEGYÜLETEK – SZINTÉZISEK

CARBON σ -DONORS – THE SYNTHESIS OF METAL ALKYL AND ARYLS

3) Fém + Hg-alkil/aryl (fém-fém csere)

Reaction of a Metal with a Mercury Alkyl or Aryl

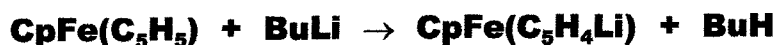
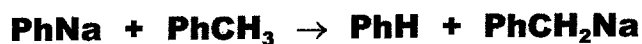


M = 1., 2., 13 csoport fémei/ 1., 2., and 13. group elements

Oldószermentes eljárás! – *Solvent free preparation!*

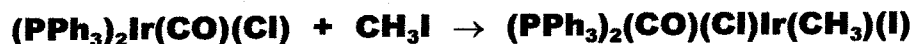
4) Fém – hidrogén csere

Metal – Hydrogen Exchange



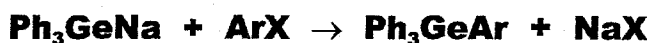
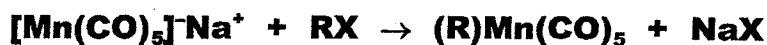
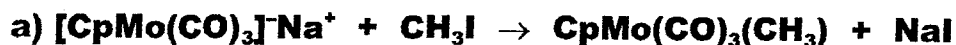
5) Oxidatív addíció

Oxidative Addition



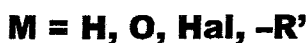
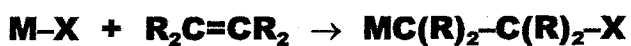
6) Fémtartalmú anion + szerves halogenid

Reactions of Metal-Containing Anions with Organic Halides



7) Fémvegyületek addíciója telítetlen kötésre (beékelődés)

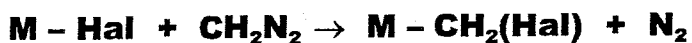
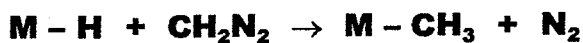
Addition of Metal Complexes to Unsaturated Substrates (insertion)



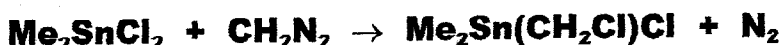
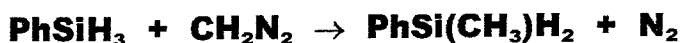
„Hidroborálás” / „Hydroboration”

8) FO vegyület + karbén

OM Compound + Carbene



Pl./e.g.



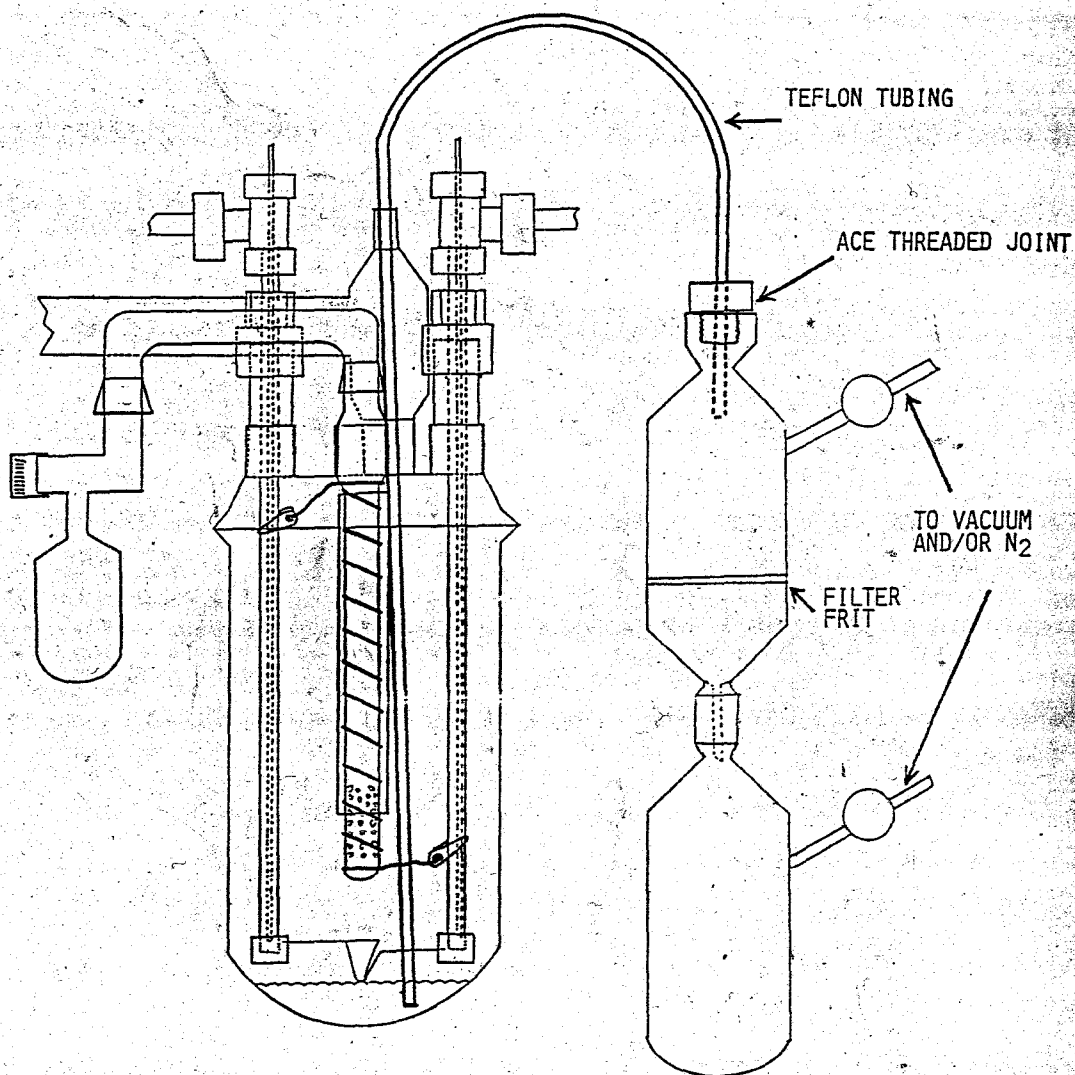
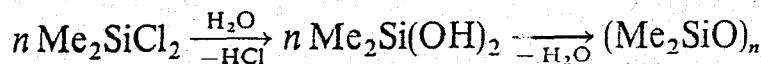
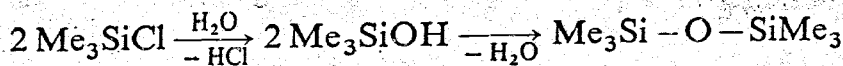
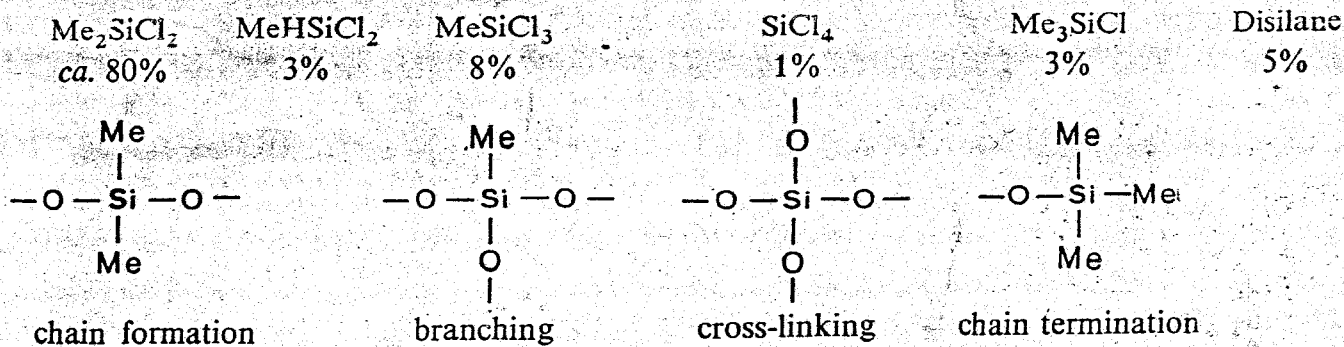
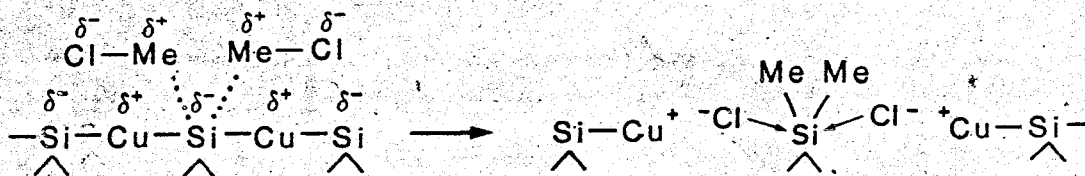
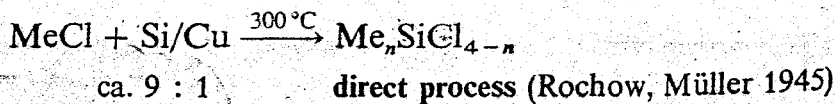


Figure 1. The slurried reaction product is transferred aerobically to the filter frit by applying a slight vacuum.

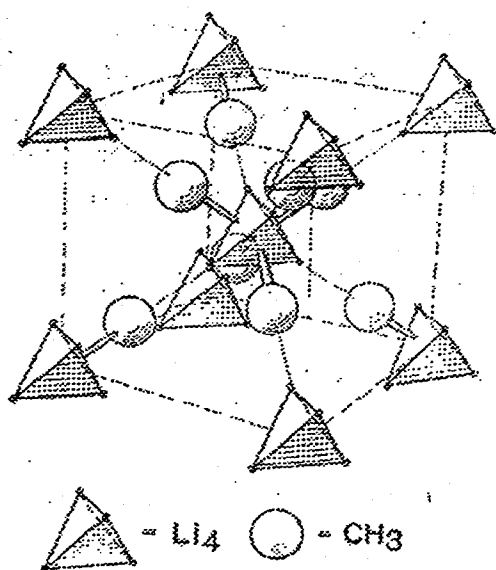
FOKI/20.

MÜLLER, R.: metil-klór-szilánok közvetlen (direkt) szintézise (1943)

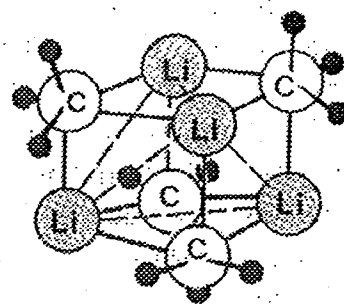


$(\text{R}_2\text{SiO})_n$ (polysilicoketones)

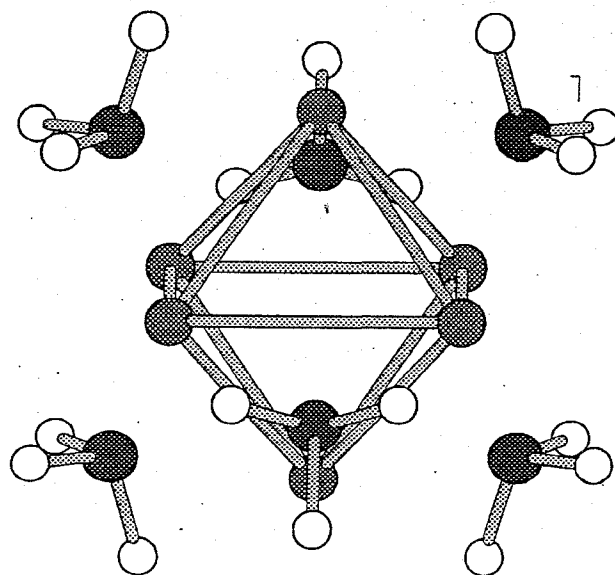
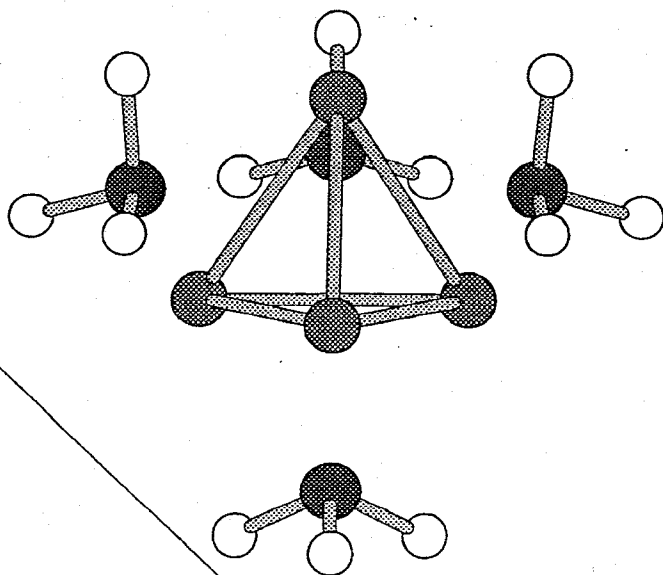
(a) Unit cell of $(\text{LiCH}_3)_4(\text{s})$.

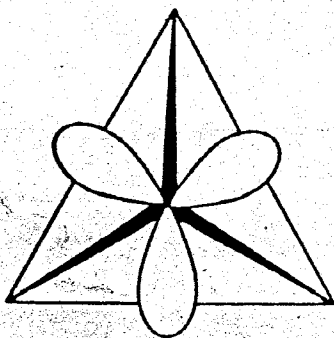


(b) Schematic drawing of the unit $(\text{LiCH}_3)_4$.

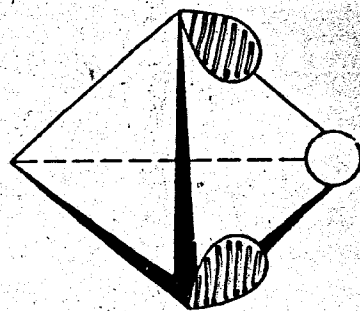
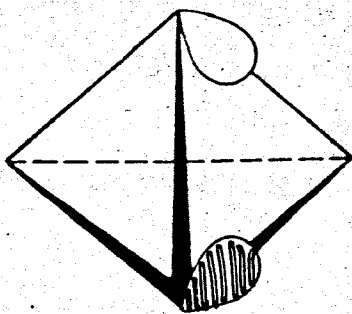
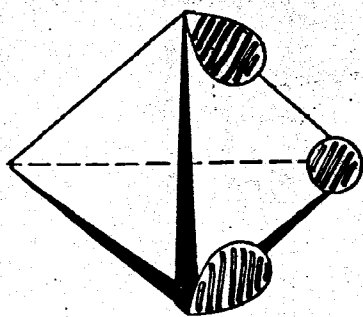


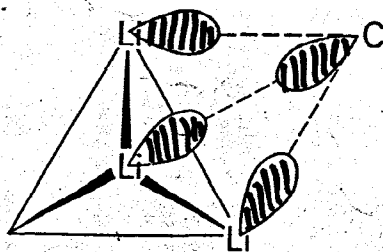
$d(\text{Li}-\text{C}) = 231 \text{ pm}$ $(\text{LiCH}_3)_4$
 $d(\text{Li} \cdots \text{C}) = 236 \text{ pm}$ $(\text{LiCH}_3)_4$
 $d(\text{Li}-\text{Li}) = 268 \text{ pm}$ $(\text{LiCH}_3)_4$
 compare: $d(\text{Li}-\text{Li}) = 267 \text{ pm}$ $\text{Li}_2(\text{g})$
 $d(\text{Li}-\text{Li}) = 304 \text{ pm}$ $\text{Li}(\text{m})$
 $r_{\text{cov}}(\text{Li}) = 134 \text{ pm}$ } 211 pm
 $r_{\text{cov}}(\text{C}) = 77 \text{ pm}$



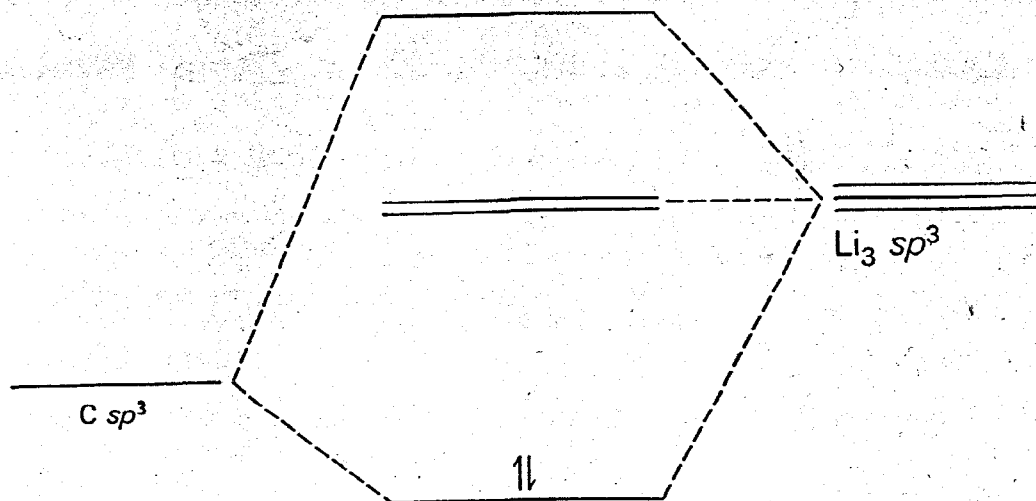


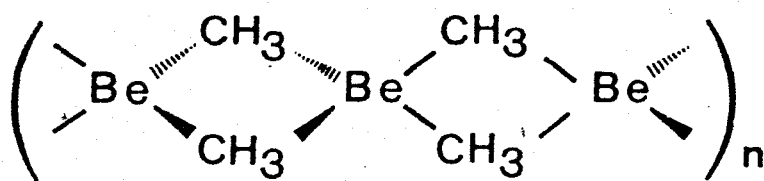
Li sp^3





4c/2e





$d(\text{Be}-\text{Be}) = 210 \text{ pm}$,
 $\text{angle Be}-\text{C}-\text{Be} = 66^\circ$
 (Rundle, 1951).

$\langle (\text{C}-\text{Be}-\text{C}) = 114^\circ \rangle > 109^\circ \Rightarrow \text{Be} \cdots \cdots \text{Be} \quad 210 \text{ pm}$

$\langle (\text{Be}-\text{C}-\text{Be}) = 66^\circ$

$d(\text{Be}-\text{C}) = 193 \text{ pm}$

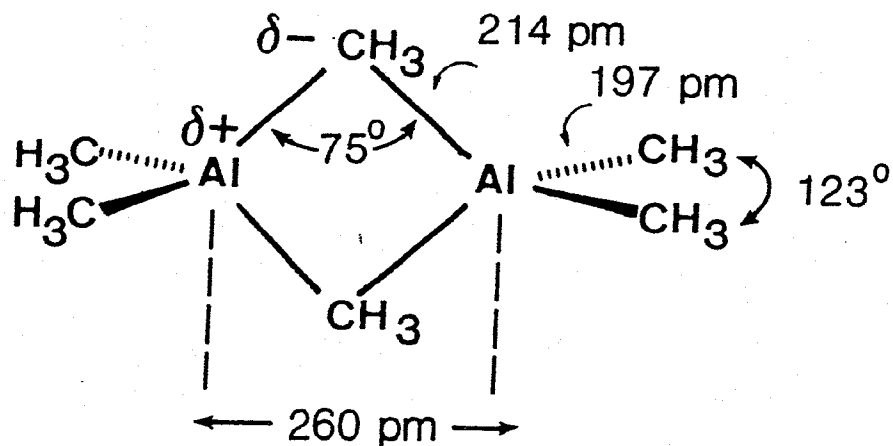
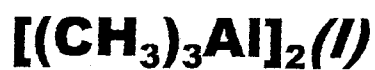
$r_{\text{cov}}(\text{Be}) = 91 \text{ pm}$

$r_{\text{cov}}(\text{C}) = 77 \text{ pm}$

$r_{\text{cov}}(\text{Be}) + r_{\text{cov}}(\text{C}) = 168 \text{ pm} < 193 \text{ pm}$

2 e - 3c kötés

2 e - 3c bond



$d(\text{Al}-\text{C}_t) = 197 \text{ pm}$

$d(\text{Al}-\text{C}_b) = 214 \text{ pm}$

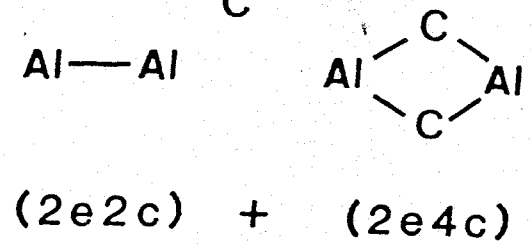
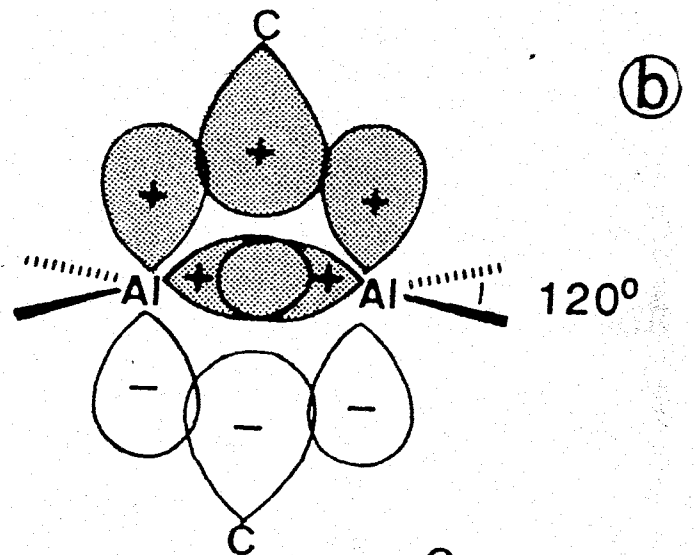
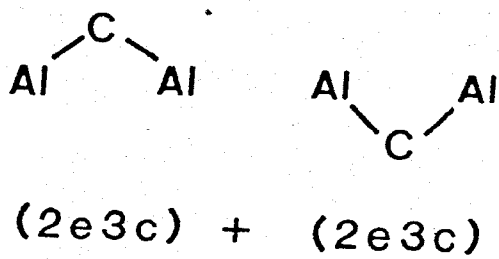
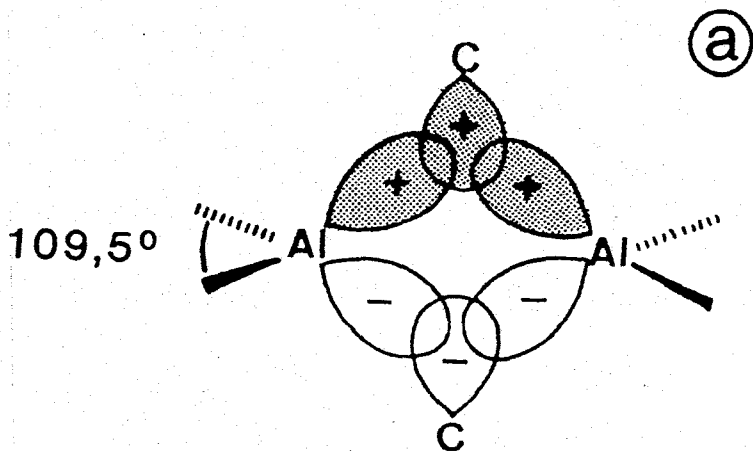
$\angle(\text{Al}-\text{C}_b-\text{Al}) = 75^\circ$

$\angle(\text{C}_t-\text{Al}-\text{C}_t) = 123^\circ$

$d(\text{Al}-\text{Al}) = 260 \text{ pm} < d(\text{Al}-\text{Al}) / \text{Al}_2\text{Cl}_6 = 340 \text{ pm}$

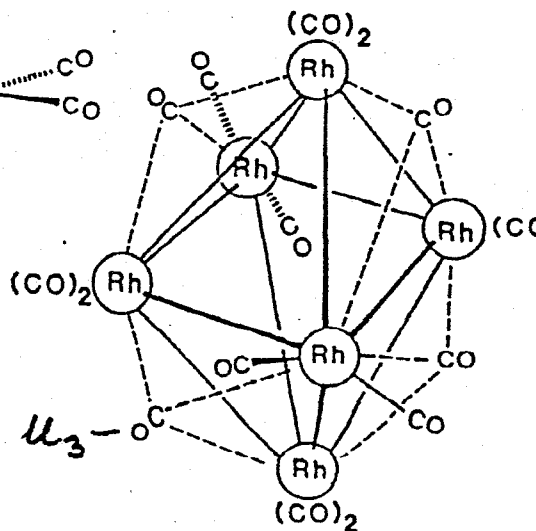
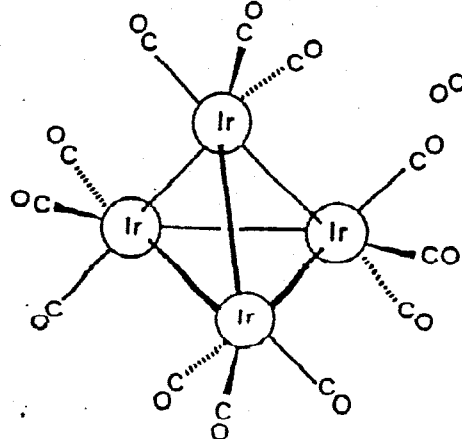
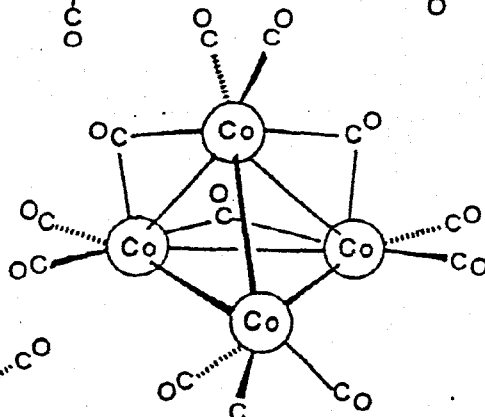
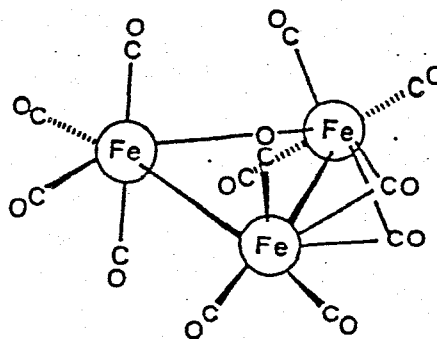
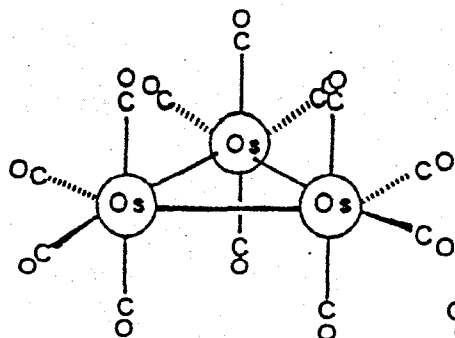
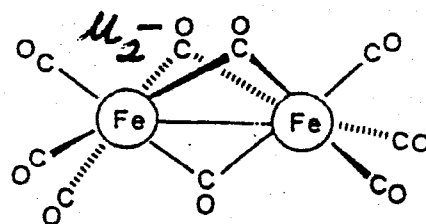
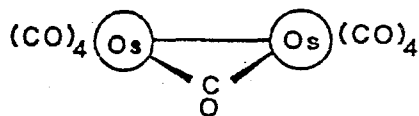
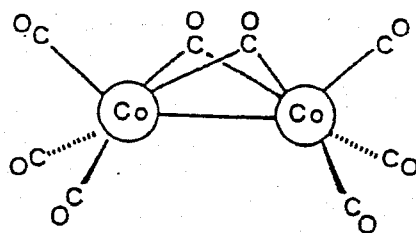
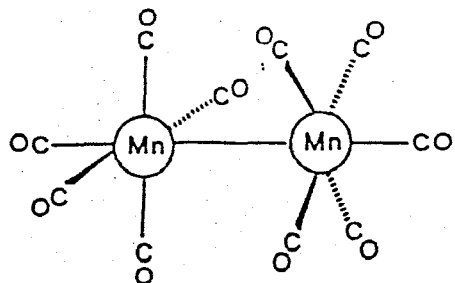
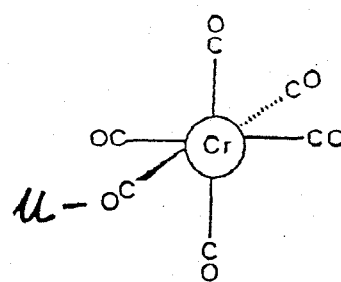
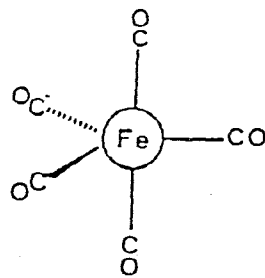
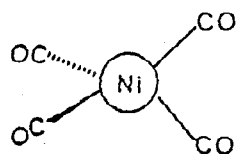
$r_{\text{cov}}(\text{Al}) = 126 \text{ pm}$

$[(\text{CH}_3)_3\text{Al}]_2(I)$



4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$ $Co_6(CO)_{16}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$ $Tc_3(CO)_{12}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$ $Ru_6(CO)_{18}$	$Rh_2(CO)_8$ $Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$ $Ir_6(CO)_{16}$	Pt	Au

Biner fémkarbonilok szerkezete



A 18 (16) ELEKTRONOS SZABÁLY

Az átmenetifémek stabilis fémorganikus vegyületeiben a vegyértékelektronok száma 18 (néhány kivételtől eltekintve).

Példák:

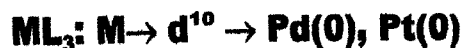
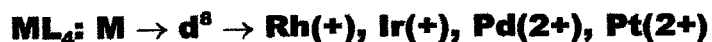


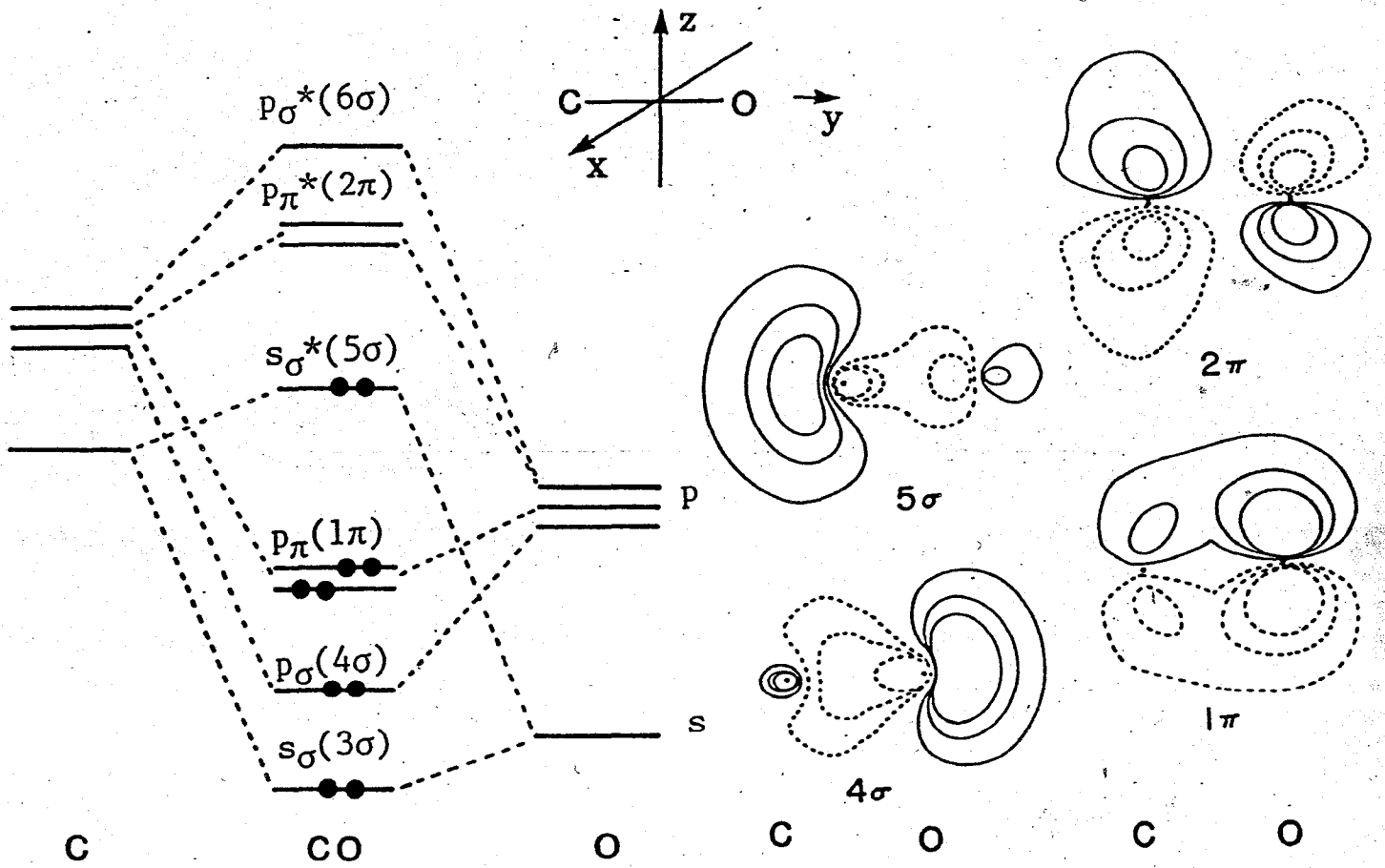
Esetenként 16 vegyértékelektronos molekulák éppen olyan stabilisak, mint ugyanannak a fémnek a 18 elektronos származékai.

Ez leginkább a d-mező jobb alsó blokkjában elhelyezkedő fémekre

igaz: Rh, Pd, Ir, Pt

Példák:





A fém – CO kötés

The metal – CO bond

Koordináció

Viszontkoordináció

Co-ordination

Back donation

$M(\sigma) \leftarrow CO(5\sigma)$

$M(\pi) \rightarrow CO(2\pi)$

σ -donor/ σ -donation

π -akceptor/ π -acceptor

M – C kötésrend

NŐ

NŐ

M – C bond order

INCR.

INCR.

C – O kötésrend

NŐ

CSÖKKEN

C – O bond order

INCR.

DECR.

$\nu(C \leftrightarrow O)$

NŐ/ INCR.

CSÖKKEN/ DECR.

$\nu(C \leftrightarrow O)/cm^{-1}$

izolált molekula: 2143

M – CO: 1850-2120

free molecule

complex

A fém – CO kötés

The metal – CO bond

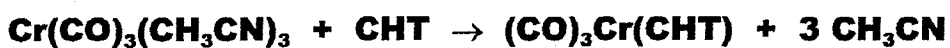
Példák/ Examples

	Ni(CO)₄	2060 cm⁻¹
d¹⁰	Co(CO)₄⁻	1890 cm⁻¹
	Fe(CO)₄²⁻	1790 cm⁻¹
	Mn(CO)₆⁺	2090 cm⁻¹
d⁶	Cr(CO)₆	2000 cm⁻¹
	V(CO)₆⁻	1860 cm⁻¹
	CO(g)	2143 cm⁻¹

A fémkarbonilok tipikus reakciói

Typical reactions of metal carbonyls

1) Szubsztitúció/ Substitution (ΔT , $h\nu$)



(Lewis bázisok, olefinek, arének/ Lewis bases, olefines, arenes)

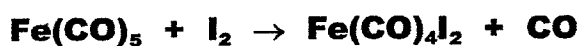
2) Nukleofil addíció/ Nucleophile addition



3) Diszproporció/ Disproportion



4) Oxidatív dekarbonilezés/ Oxidative decarbonylation

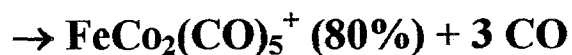


Fémkarbonilok szerepe a katalízis-kutatásban

(Gázfázisú ionkémia)

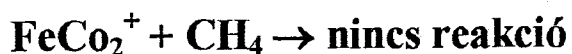
FTMS + Collision Induced Dissociation (CID)

Példa: C – H kötés aktiválása alkánokban $[\text{FeCo}_2]^+$ klaszterrel



↓

CID (Ar*)

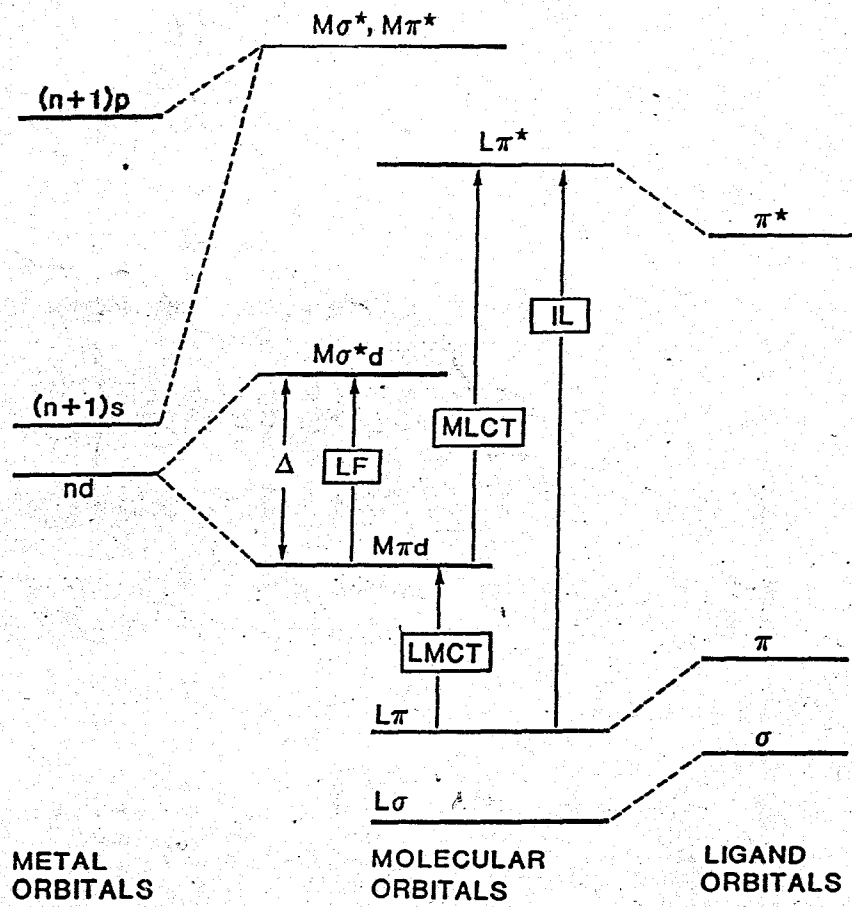


↓

CID (Ar*)

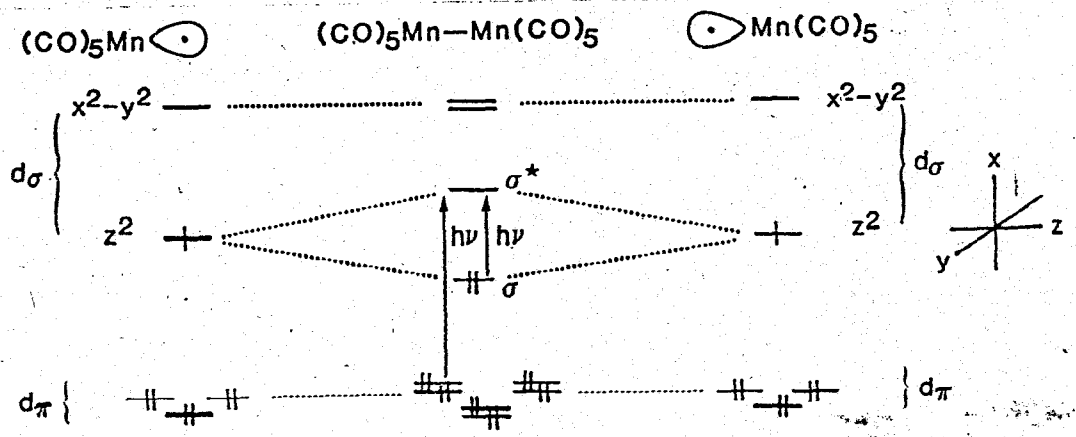


	IE₁(M_(g))/eV	IE₁(M(CO)_{6(g)})/eV	D(M-CO)	ν(C↔O)
			kcal/mol	cm⁻¹
Cr	6,76	8,15	27	2000
Mo	7,38	8,23	36	1984
W	7,98	8,56	42	1960



MLCT

Fem-fem kötés hasadós



FOKI/37.

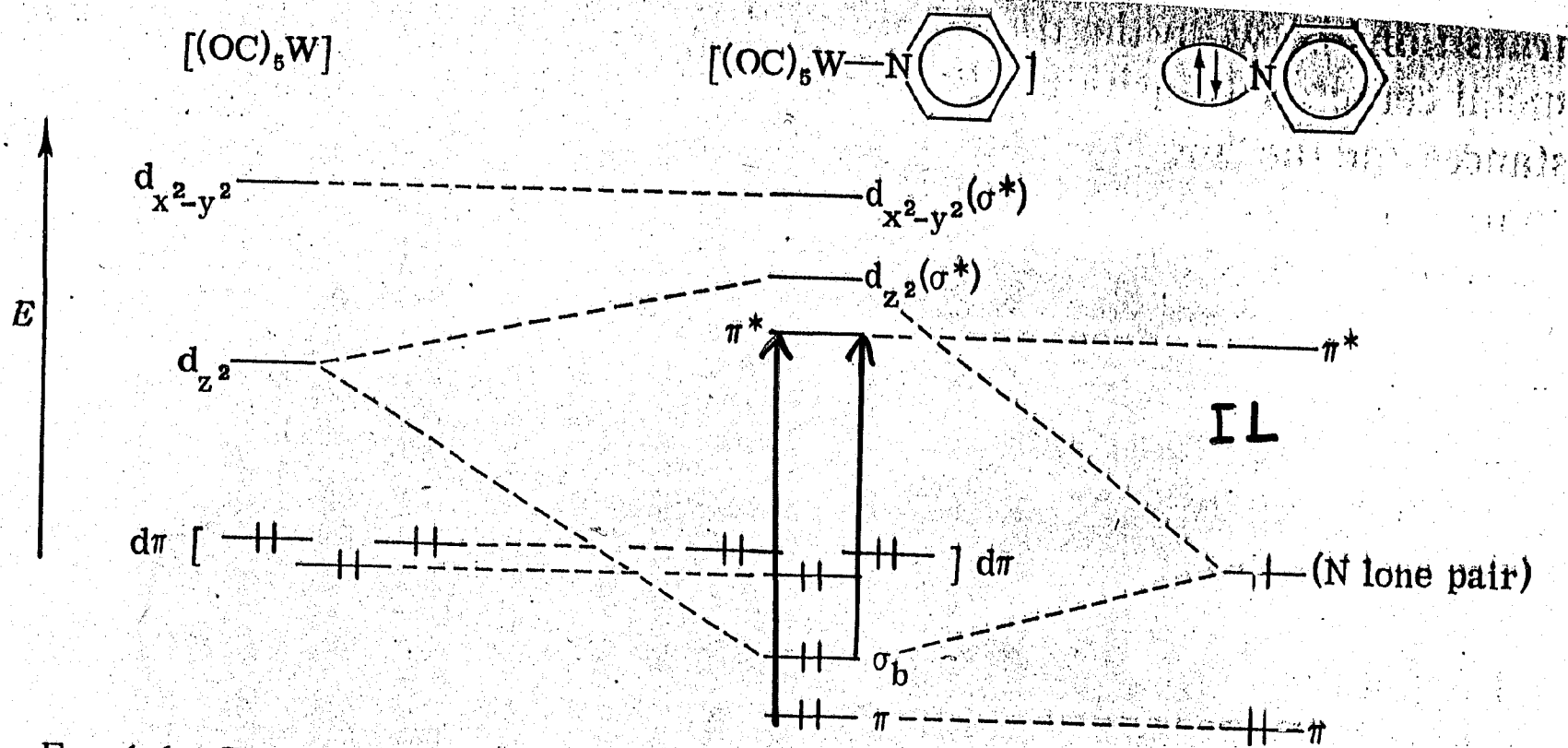


FIG. 1-6. Perturbation of pyridine electronic structure via σ bonding to $[W(CO)_5]$.

IV. Excited States of Organometallic Complexes

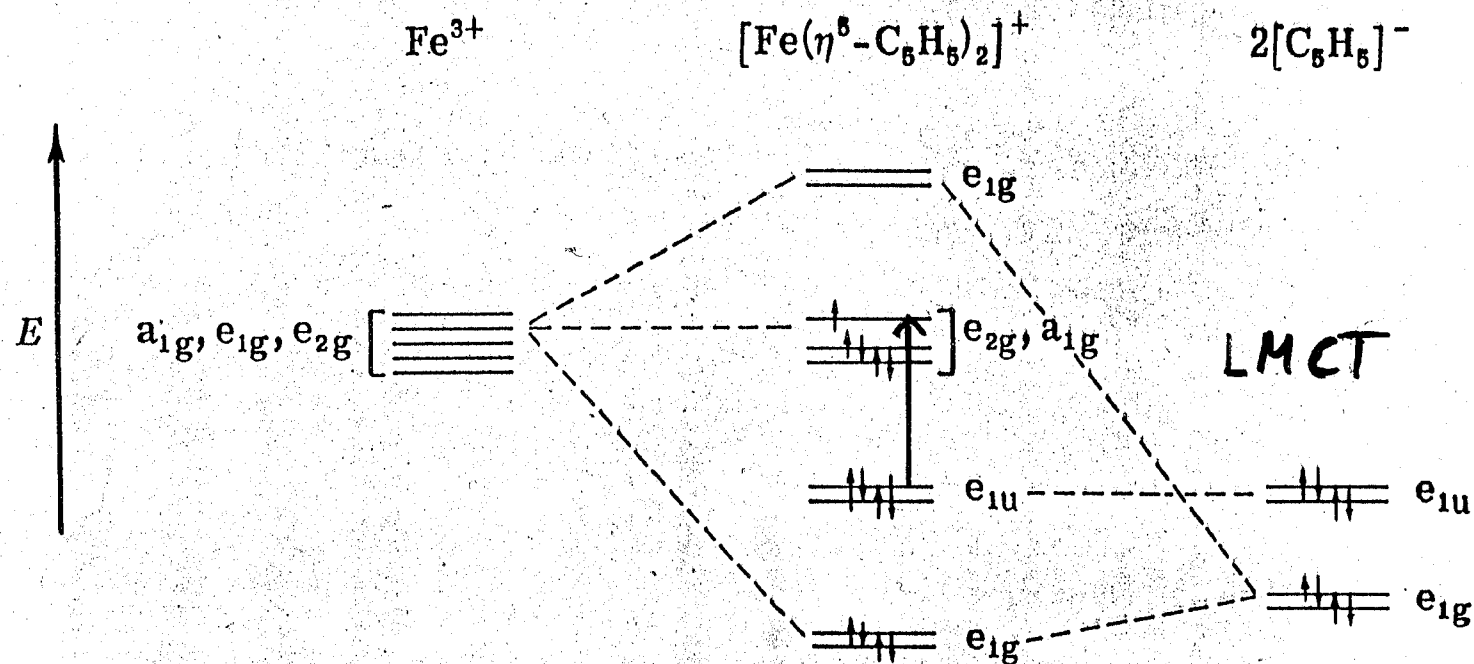


FIG. 1-11. One-electron levels for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+$.

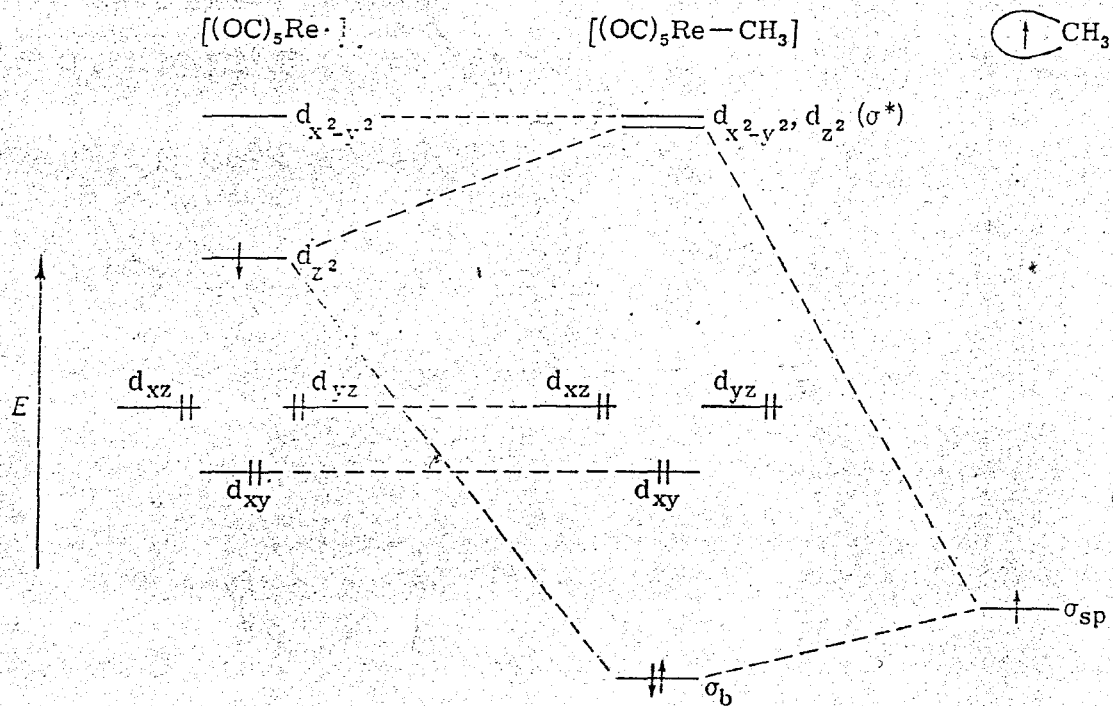


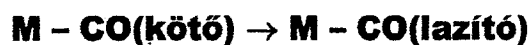
FIG. 1-12. One-electron level scheme for $[\text{Re}(\text{CO})_5\text{CH}_3]$.

Fotokémia: preparatív alkalmazások

1) Fémkarbonilok fotokémiai szubsztitúciója



Elektrongerjesztés: „Ligand Field” (LF); $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$



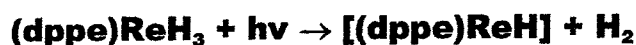
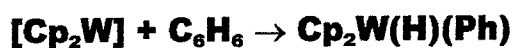
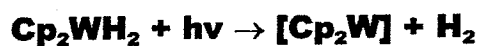
Reakciósebesség: $k(\text{fotongerjesztés}) > k(\text{termikus gerjesztés})$

2) Fém - fém kötéshasítása



Elektrongerjesztés: $\sigma \rightarrow \sigma^*$ átmenet

3) Fém-hidrogén kötés hasítása



(bisz-difenilfoszfino-etán)

Fotokémia: preparatív alkalmazások (folyt.)

4) Fém - szén kötés hasítása

a) σ - π átrendeződés (π - allil-komplexek)



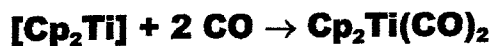
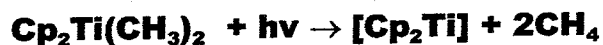
σ -komplex/18 VE

átmeneti komplex/16 VE



π -komplex (η^3 -allil-)/18 VE

b) Fotodezalkilezés



c) Fischer-Müller reakció

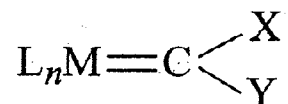
Arén- és olefin-komplexek előállítása M - C σ -kötés hasításával

M = V, Cr, Fe, Ru, Os, Pt; R = i -Pr-csoport

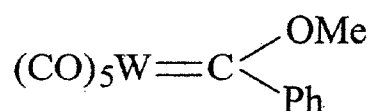


átmeneti komplex: $[(i\text{Pr})_2\text{Fe}(\text{H})(\pi-\text{C}_3\text{H}_6)]$

Átmenetifém-karbének (1)



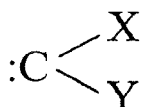
X, Y = alkil, aril, H, O, S, N, halogének



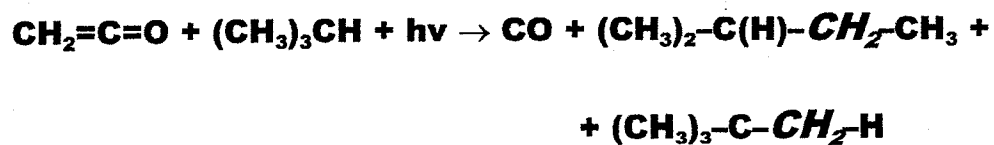
Fischer - f. karbén (1964)



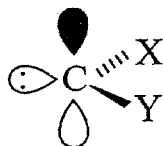
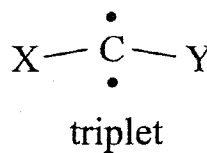
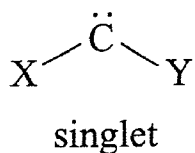
Schrock - f. karbén (1975)



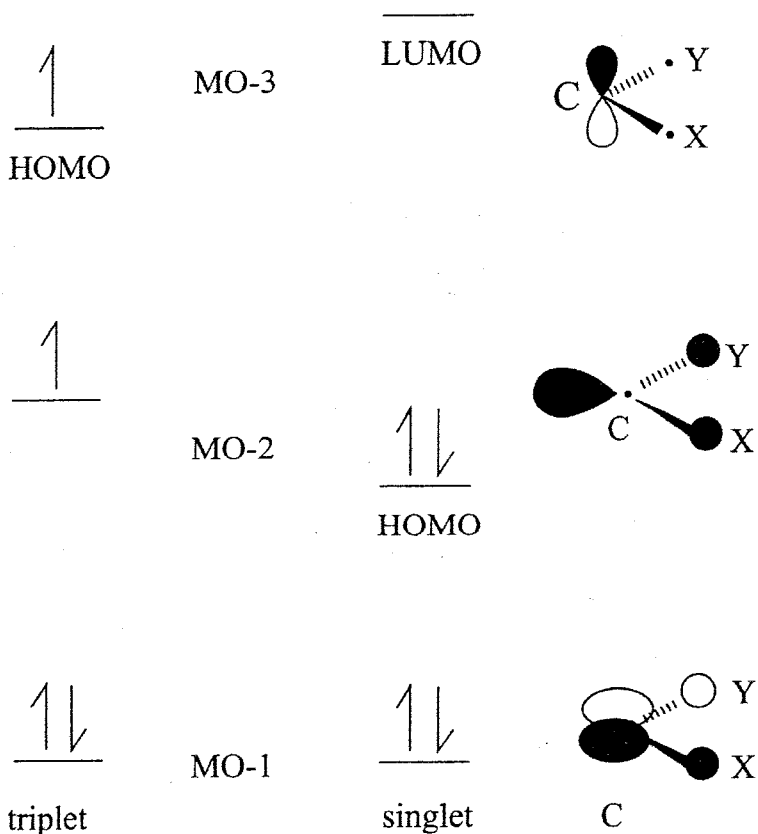
Nagy reakcióképesség; pl. beékelődés a C -C, vagy C-H kötésbe:



Átmenetifém-karbének (2)



Karbén molekulapályák

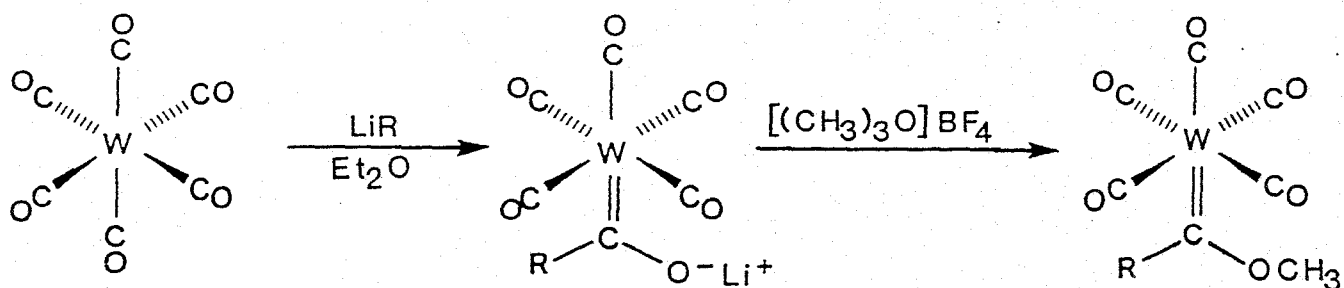


X, Y = H, alkyl (typically a triplet)

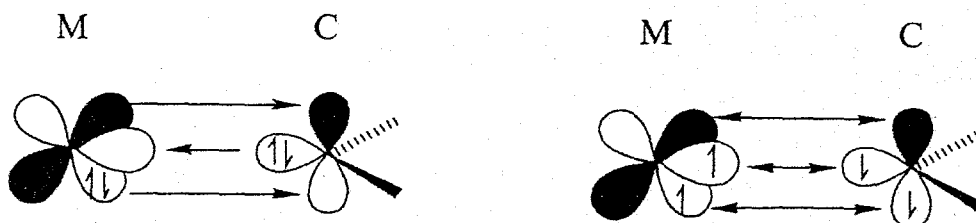
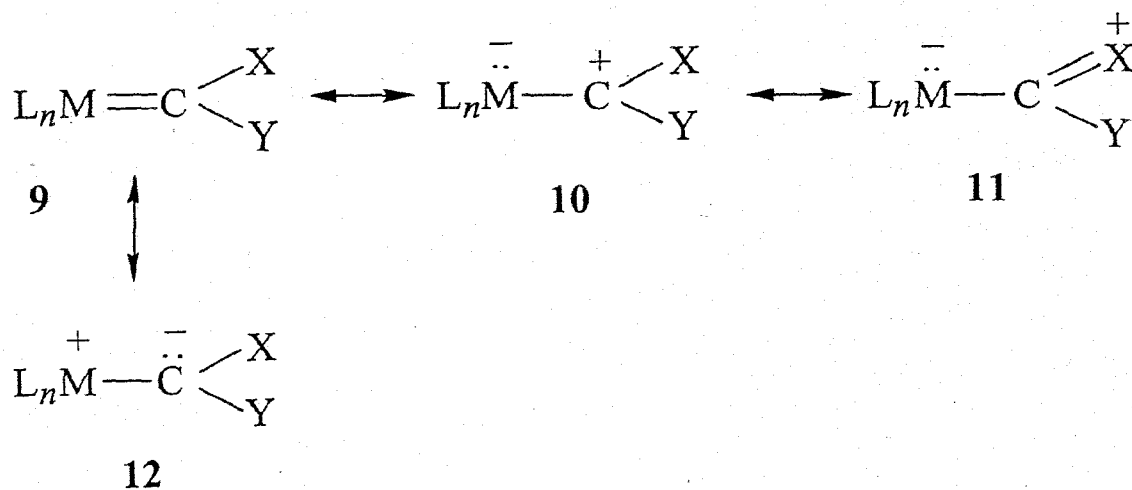
X, Y = Cl, O, N, S (typically a singlet)

Átmenetifém-karbének (3)

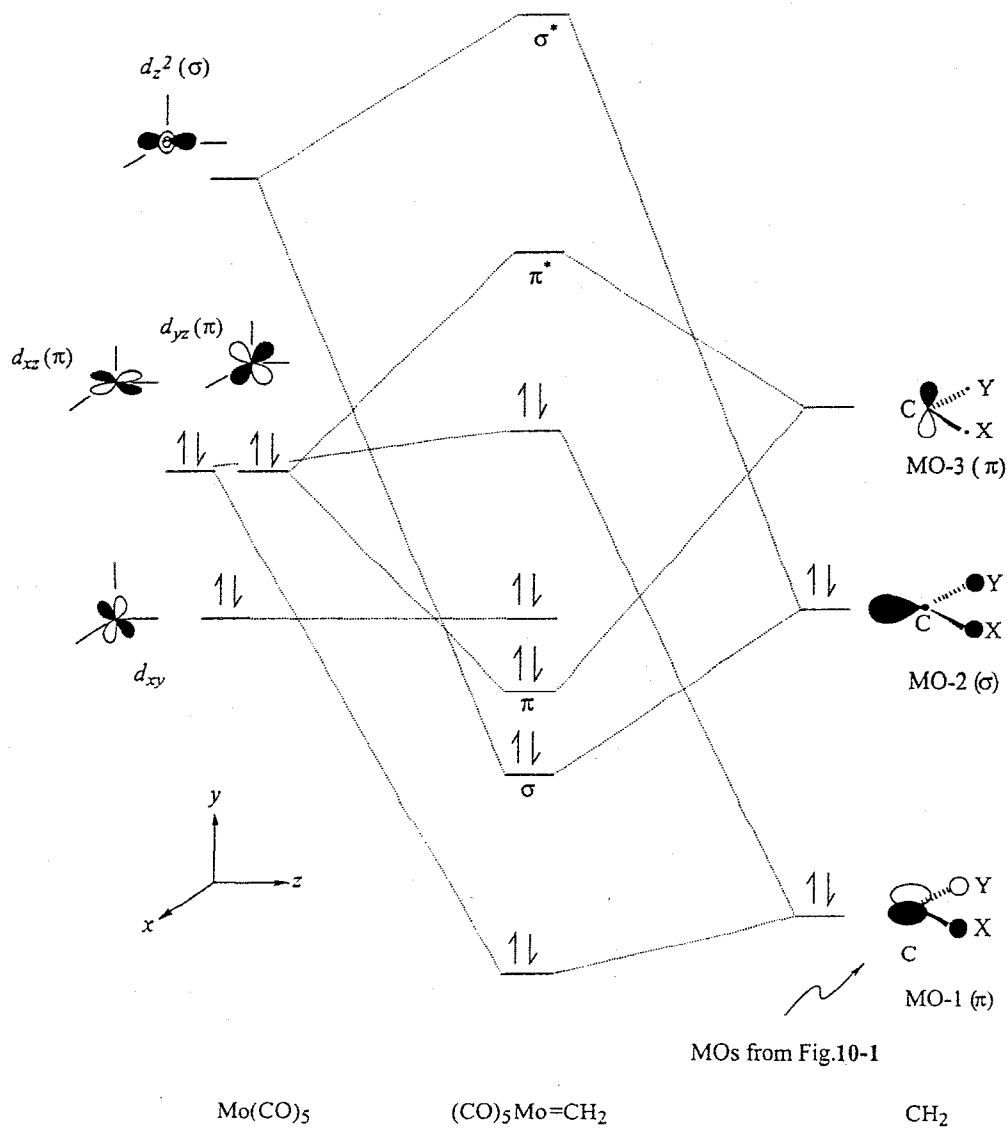
(E. O. Fischer, 1964)



This reaction is concordant with quantum-chemical calculations (Fenske, 1968), which have shown that the carbon atom in coordinated CO should bear a larger positive charge than in free CO. Nucleophilic attack should therefore be favorable.

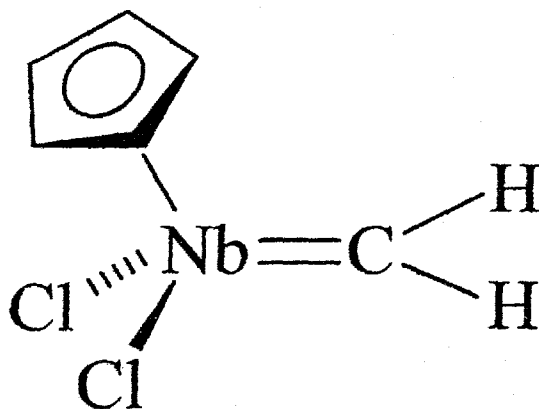


Átmenetifém-karbének (4)



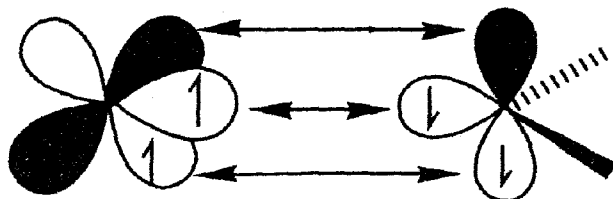
Átmenetifém-karbének (5)

Schrock - f. karbén (alkilidén)



M

C



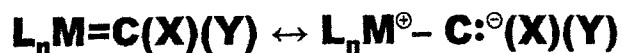
$d(yz)$

$2p(y)$

$d(z^2)$

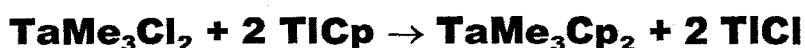
$2p(z)$

A karbén C-atom nukleofil reakciócentrum:



Átmenetifém-karbének (5.a)

Schrock – f. karbén – előállítás



Elektrofil Me-hasítás $\text{Ph}_3\text{C}^\oplus$ (trityl)-kationnal:



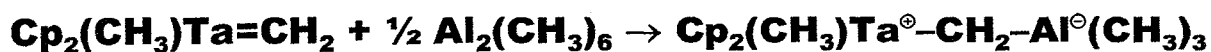
H hasítás α -szénatomról erős bázissal (metilén-trifenil-foszfórán):



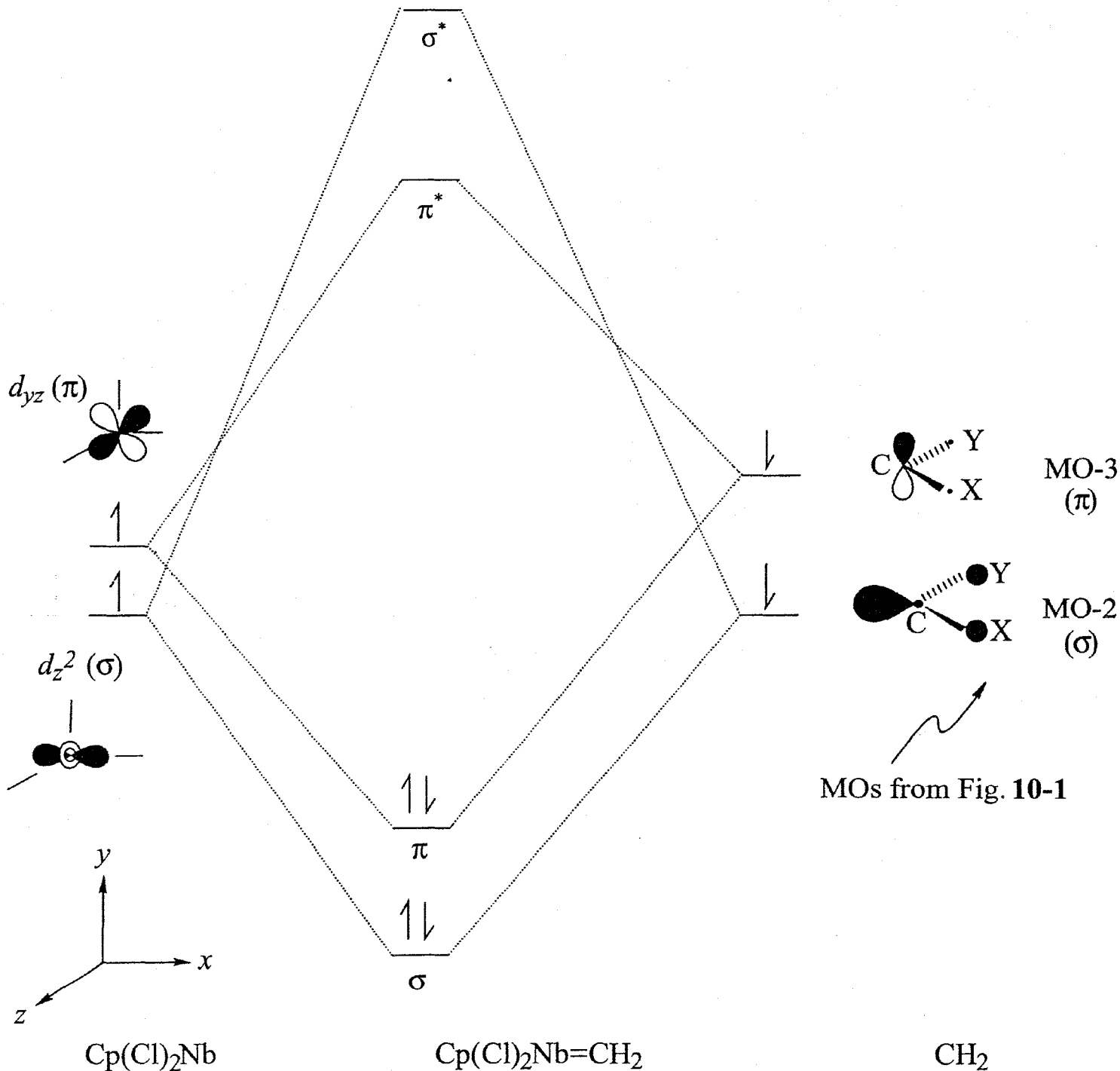
+



Elektrofil reakció a C(karbén)-atomon

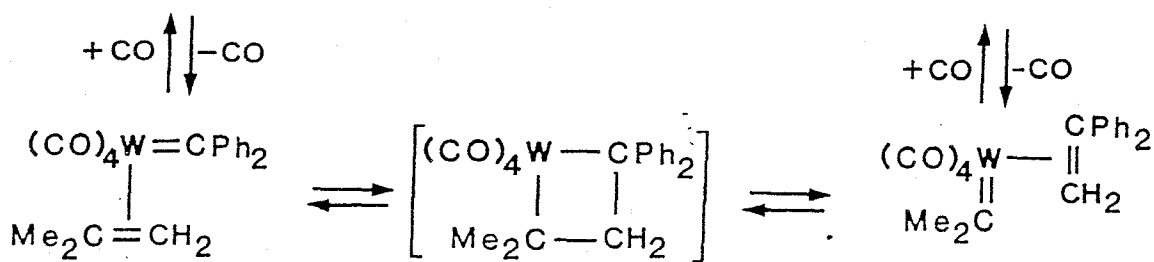
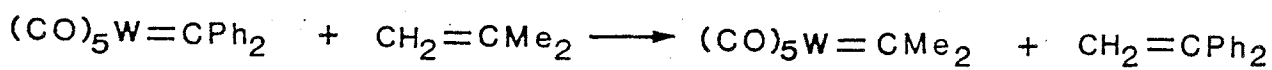
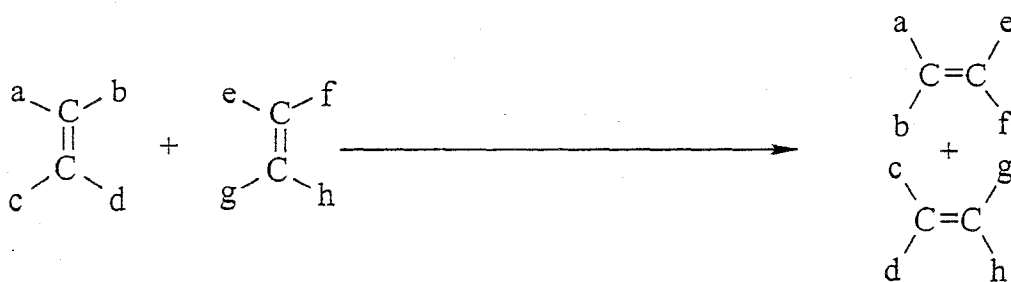
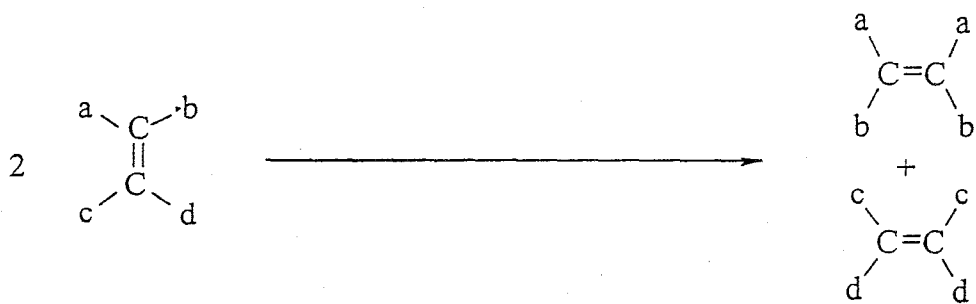


Átmenetifém-karbének (6)



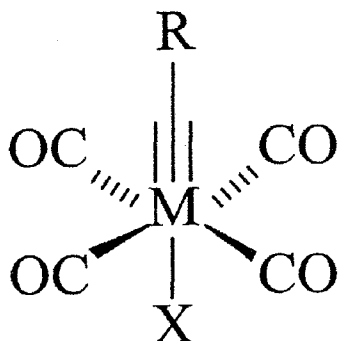
Fischer- és Schrock-féle átmenetifém karbén-komplexek

Jellemző tulajdonság	Fischer-típusú	Schrock-típusú
Központi fém [ox. állapot]	„középső/kései” [Fe(0), Mo(0), Cr(0)]	„korai” átmenetifém [Ti(IV), Ta(V)]
Szubsztituens/ $C_{\text{karbén}}$	elektronegatív atom Pl. O, vagy N	H, vagy R
Egyéb ligandumok	Jó π -akceptor Pl. CO	Jó σ -, vagy π -donor Pl. Cp, Cl, alkil
VE száma	18 e	10-18 e
$C_{\text{karbén}}$	elektrofil	nukleofil



Átmenetifém-karbinek (1)

Fischer-f. karbin

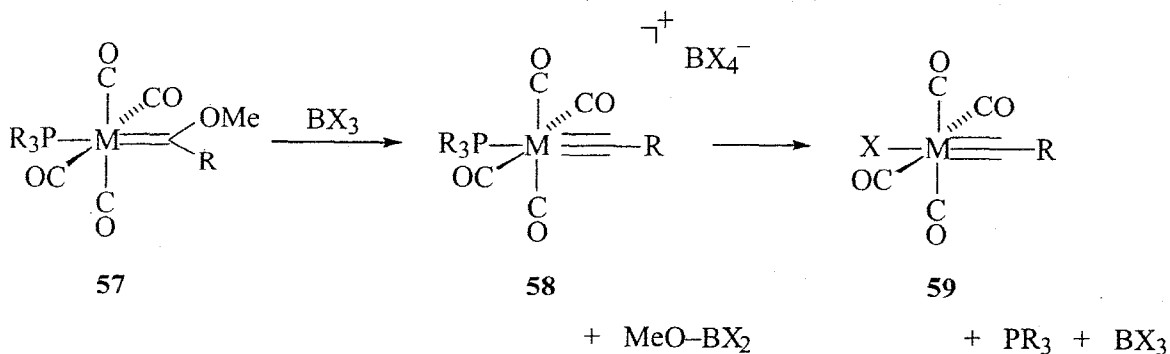


M = Cr, Mo, W

X = Cl, Br, I

R = Me, Et, Ph

Előállítás:



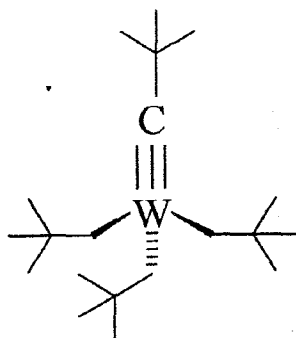
R = Alkyl, Aryl; M = Mo, W; X = Cl, Br

10.35

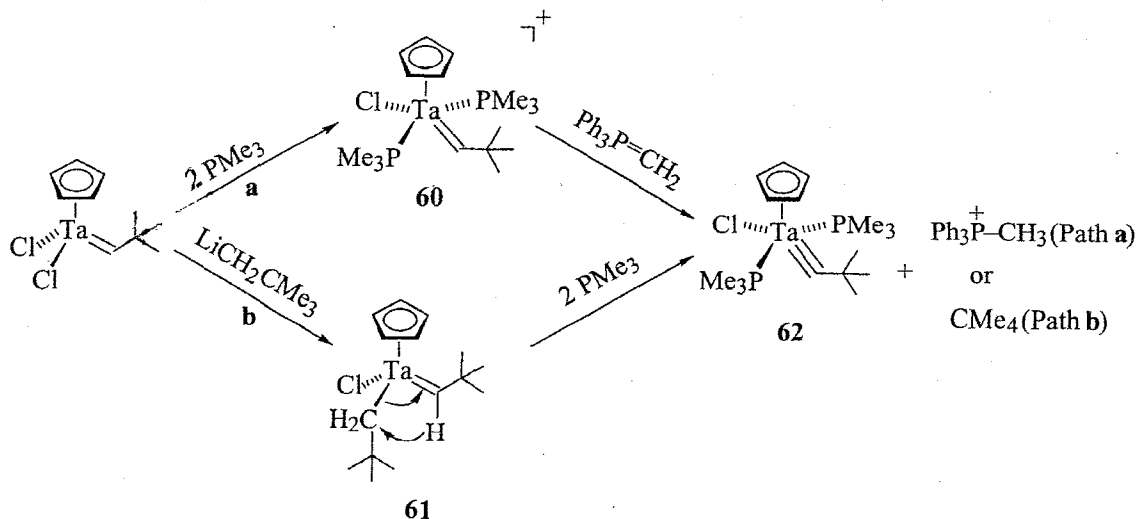
- **alkoxi csoport elektrofil hasítása; kationos karbin komplex keletkezése;**
- **foszfin - halogenid ligandumcsere (*transz*-hatás !)**

Átmenetifém-karbinek (2)

Schrock-f. karbin (alkilidin)



Előállítás:



Scheme 10.8

Two Routes to Schrock-Type
Carbyne Complexes

a) $\text{Cl}^\ominus \rightarrow 2 \text{PMe}_3$ ligandumcsere; α -deprotonálás erős bázissal (ylid);

b) $\text{Cl}^\ominus \rightarrow$ neopentil ligandumcsere; 2PMe_3 ligandum asszociáció +

+ intramolekuláris α -elimináció.

BACK BONDING

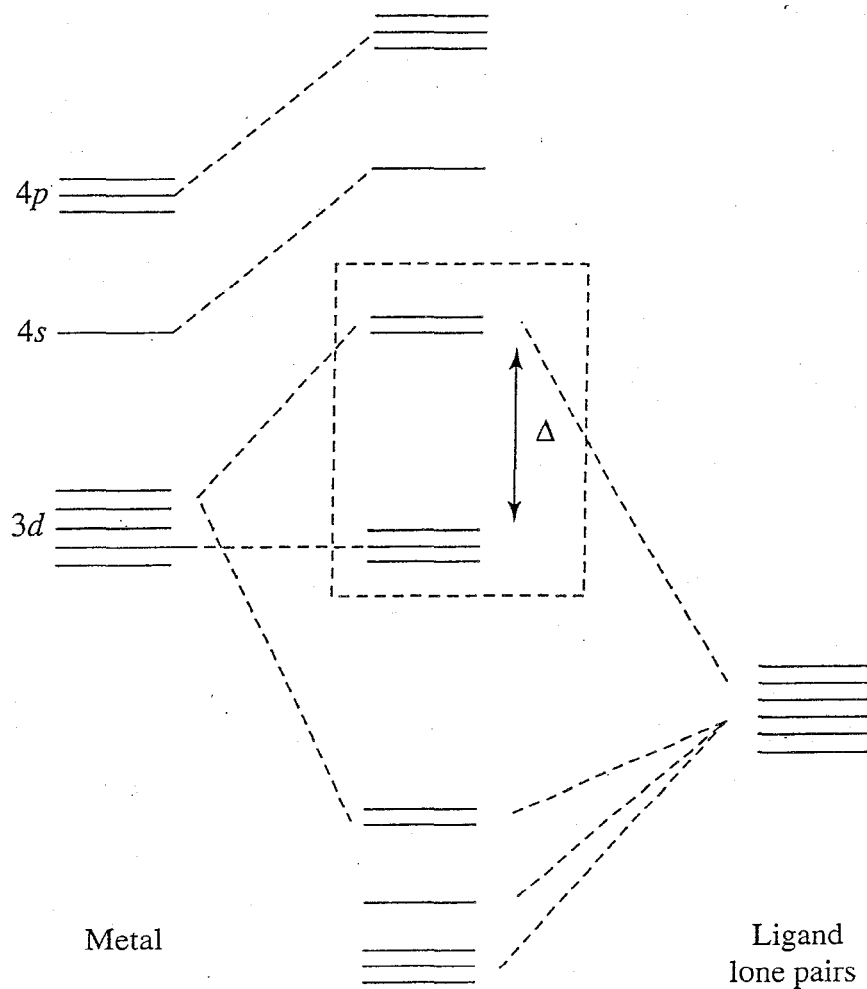


FIGURE 1.5 Molecular orbital, or ligand field picture, of metal ligand bonding in an octahedral ML_6 complex. The box contains the d orbitals.

This is why third-row metals tend to be used when isolation of stable compounds is the aim. When catalysis is the goal (Chapter 9), the intermediates involved have to be reactive and therefore relatively less stable, and first- and second-row metals are sometimes preferred.

Isoconfigurational Ions

Transition metals tend to be treated as a group rather than as individual elements. One reason is that d^n ions of the same configuration (e.g., $n = 6$) show important similarities independent of the identity of the element. This means that d^6 Co(III) is closer in properties to d^6 Fe(II) than to d^7 Co(II). The variable valency of the transition metals leads to many cases of isoconfigurational ions.

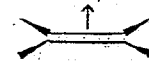


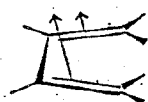
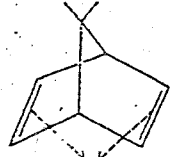
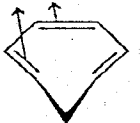

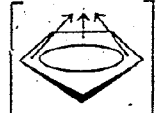

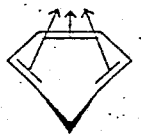

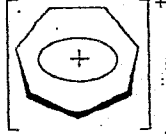
1.5 THE LIGAND FIELD

The crystal field picture gives a useful qualitative understanding, but, once having established what to expect, we turn to the more sophisticated *ligand field* model. This is really a conventional molecular orbital, or MO, picture for accurate electronic structure calculations. In this model (Fig. 1.5), we consider the s , the three p , and the five d orbitals of the valence shell of the isolated ion as well as the lone pair orbitals of a set of pure σ -donor ligands in an octahedron around the metal. Six of the metal orbitals, the s , the three p , and the two d_σ , which we will call the dsp_σ set, find symmetry matches in the six ligand lone-pair orbitals. By combining the six metal orbitals with the six ligand orbitals, we make a bonding set of six (the M-L σ bonds) that are stabilized, and an antibonding set of six (the M-L σ^* levels) that are destabilized when the six L groups approach the bonding distance. The remaining three d orbitals, the d_π set, do not overlap with the ligand orbitals, and remain nonbonding. In a d^6 ion, we have 6e (six electrons) from Co^{3+} and 12e from the ligands, giving 18e in all. This means that all the levels up to and including the d_π set are filled, and the M-L σ^* levels remain unfilled. Note that we can identify the familiar crystal field splitting pattern in the d_π and two of the M-L σ^* levels. The Δ splitting will increase as the strength of the M-L σ bonds increases. The bond strength is the analog of the effective charge in the crystal field model. In the ligand field picture, high-field ligands are ones that form strong σ bonds. We can now see that a d_σ orbital of the crystal field picture is an M-L σ -antibonding orbital.

The L lone pairs start out in free L as pure ligand electrons but become bonding electron pairs shared between L and M when the M-L σ bonds are formed; these are the 6 lowest orbitals in Fig. 1.5 and are always completely filled (12 electrons). Each M-L σ -bonding MO is formed by the combination of the ligand lone pair, $L(\sigma)$, with $M(d_\sigma)$ and has both metal and ligand character, but $L(\sigma)$ predominates. Any MO will more closely resemble the parent atomic orbital that lies closest in energy to it, and $L(\sigma)$ almost always lies below $M(\sigma)$.

Komplexek π -donor ligandumokkal (1)

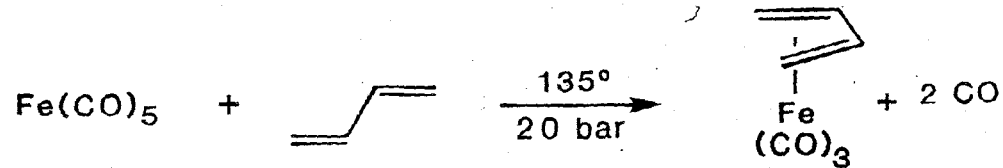
Néhány ligandum koordinációs jellemzője

Ligand	Donor Pairs	Coordination
$\eta^2\text{-C}_2\text{H}_4$ <i>→ floptocitós</i>	1	
$\eta^3\text{-C}_3\text{H}_5$ (allyl)	2	
$\eta^3\text{-C}_7\text{H}_7$ (cycloheptatrienyl)		
$\eta^4\text{-C}_4\text{H}_6$ (butadiene)		
$\eta^4\text{-C}_7\text{H}_8$ (norbornadiene)		
$\eta^4\text{-C}_7\text{H}_8$ (cycloheptatriene)		
$\eta^4\text{-C}_8\text{H}_8$ (cyclooctatetraene)		
$\eta^5\text{-C}_5\text{H}_5$ (cyclopentadienyl)	3	
$\eta^6\text{-C}_6\text{H}_6$ (benzene)		
$\eta^6\text{-C}_7\text{H}_8$ (cycloheptatriene)		
$\eta^6\text{-C}_8\text{H}_8$ (cyclooctatetraene)		
$\eta^7\text{-C}_7\text{H}_7^+$ (tropylium)		

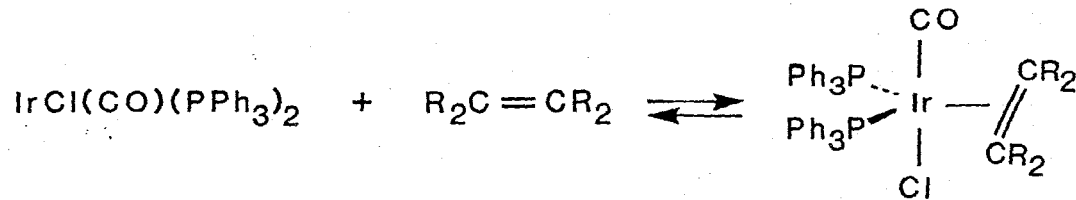
Komplexek π -donor ligandumokkal (2)

Olefin és diolefin komplexek előállítása

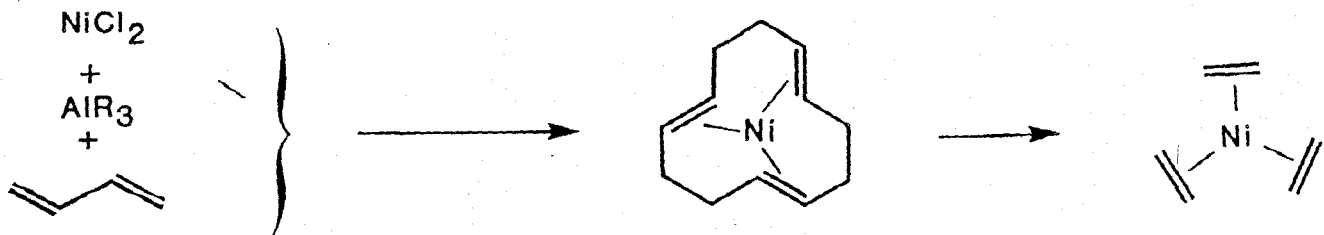
1) Szubsztitúció



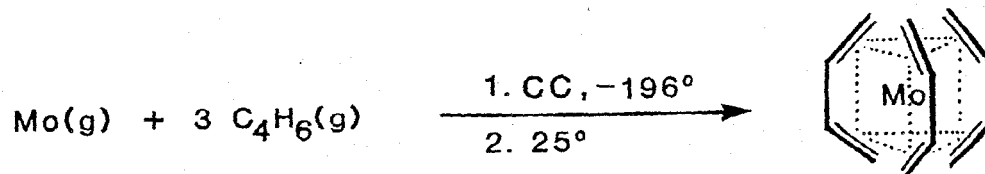
2) Addíció



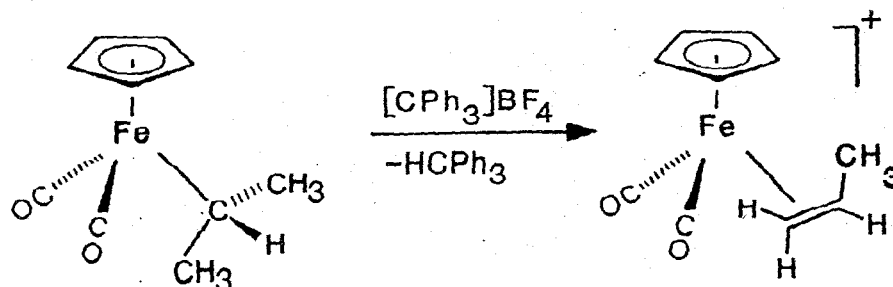
3) Fém só + olefin + redukálószer



4) CC



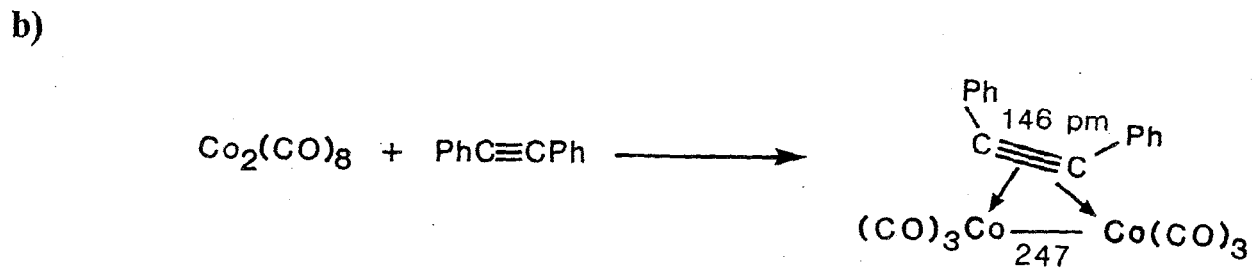
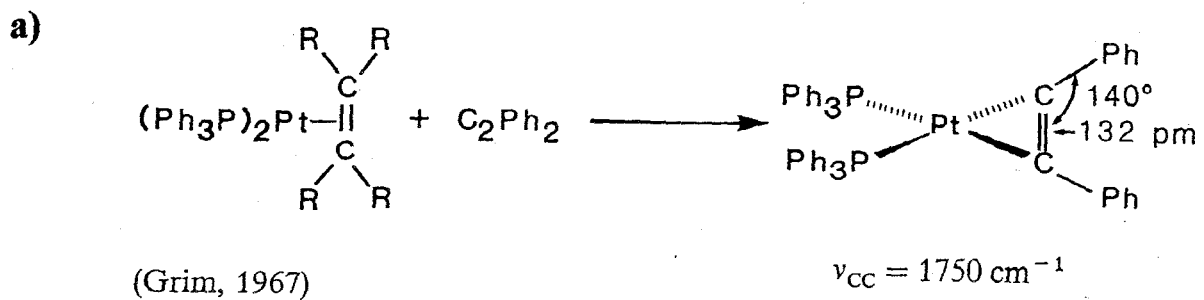
5) Hidrid-hasítás



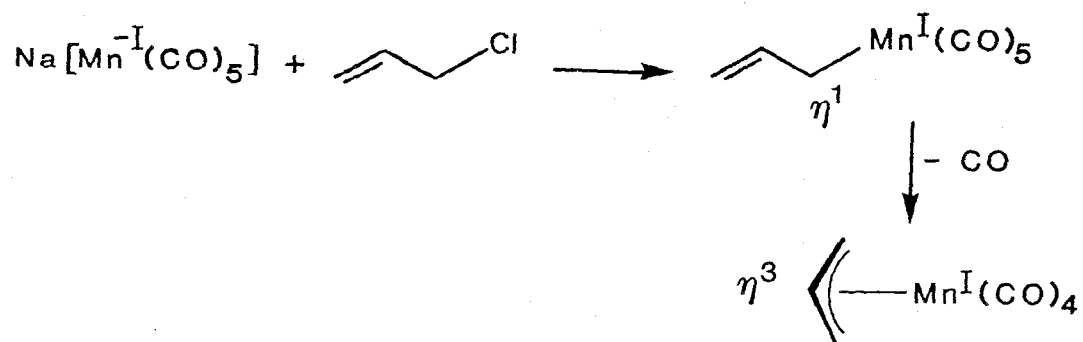
Komplexek π -donor ligandumokkal (3)

Alkin és π -allil komplexek előállítása

Alkin-komplexek: szubsztitúció



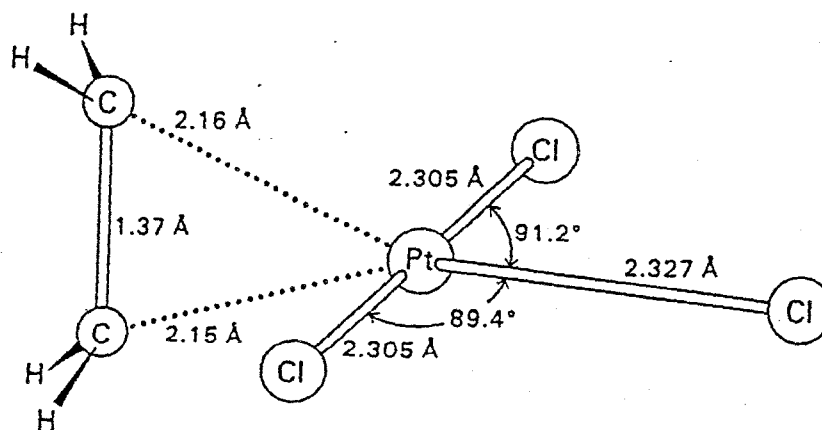
σ -allil - π -allil átrendeződés



Komplexek π -donor ligandumokkal (4)

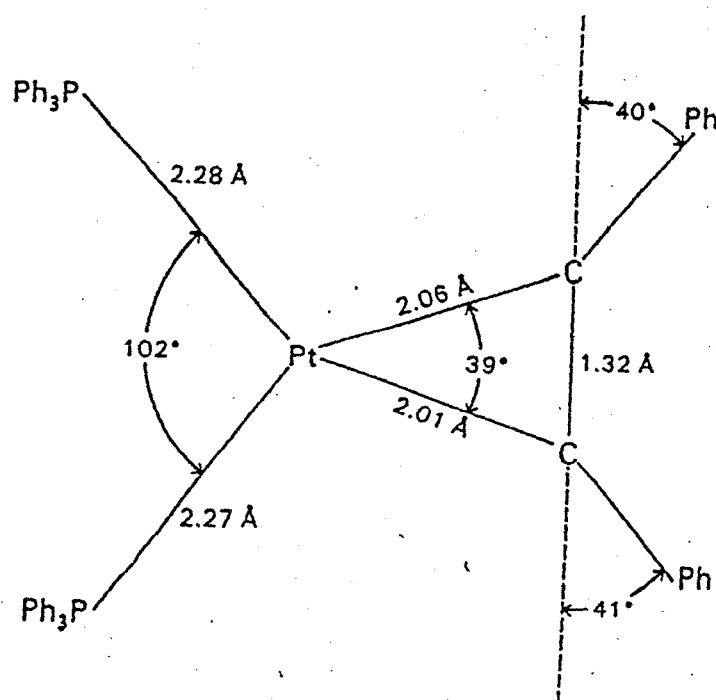
Alkén- és alkin-komplexek szerkezete

A Zeise-só



$\text{L}_3\text{M}(\text{alkén})$

Bisz-(trifenilfoszfino)-difenilacetilén-platina

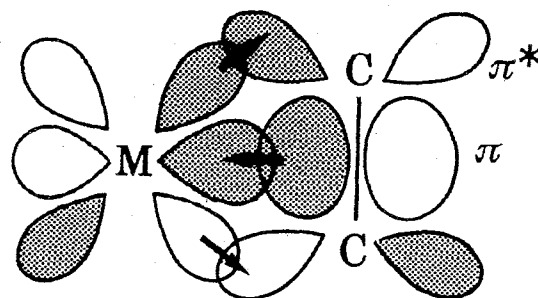


$\text{L}_2\text{M}(\text{alkin})$

Komplexek π -donor ligandumokkal (5)

A Dewar – Chatt – Duncanson (DCD) modell

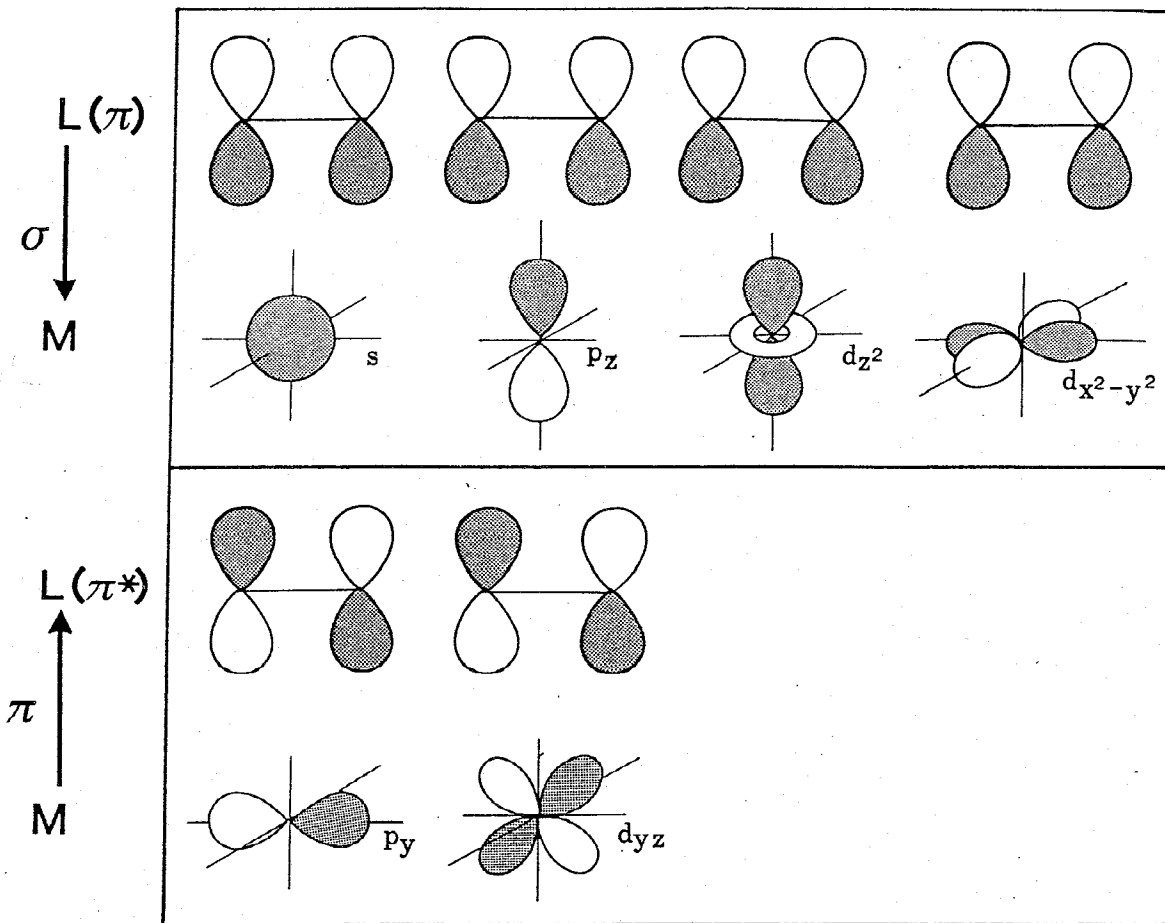
The coordination of a monoolefin to a transition metal provides the simplest example of a metal π -complex. The qualitative bonding description (Dewar, 1951; Chatt, Duncanson, 1953) is similar to that for the M – CO moiety as far as the donor-acceptor synergism is concerned.



The donor component (from the ligand's viewpoint) is the interaction of the filled, π -bonding orbital of ethylene with vacant metal orbitals, the acceptor component that of filled metal orbitals with the vacant π^ -antibonding orbital of ethylene (shading indicates orbital phases.)*

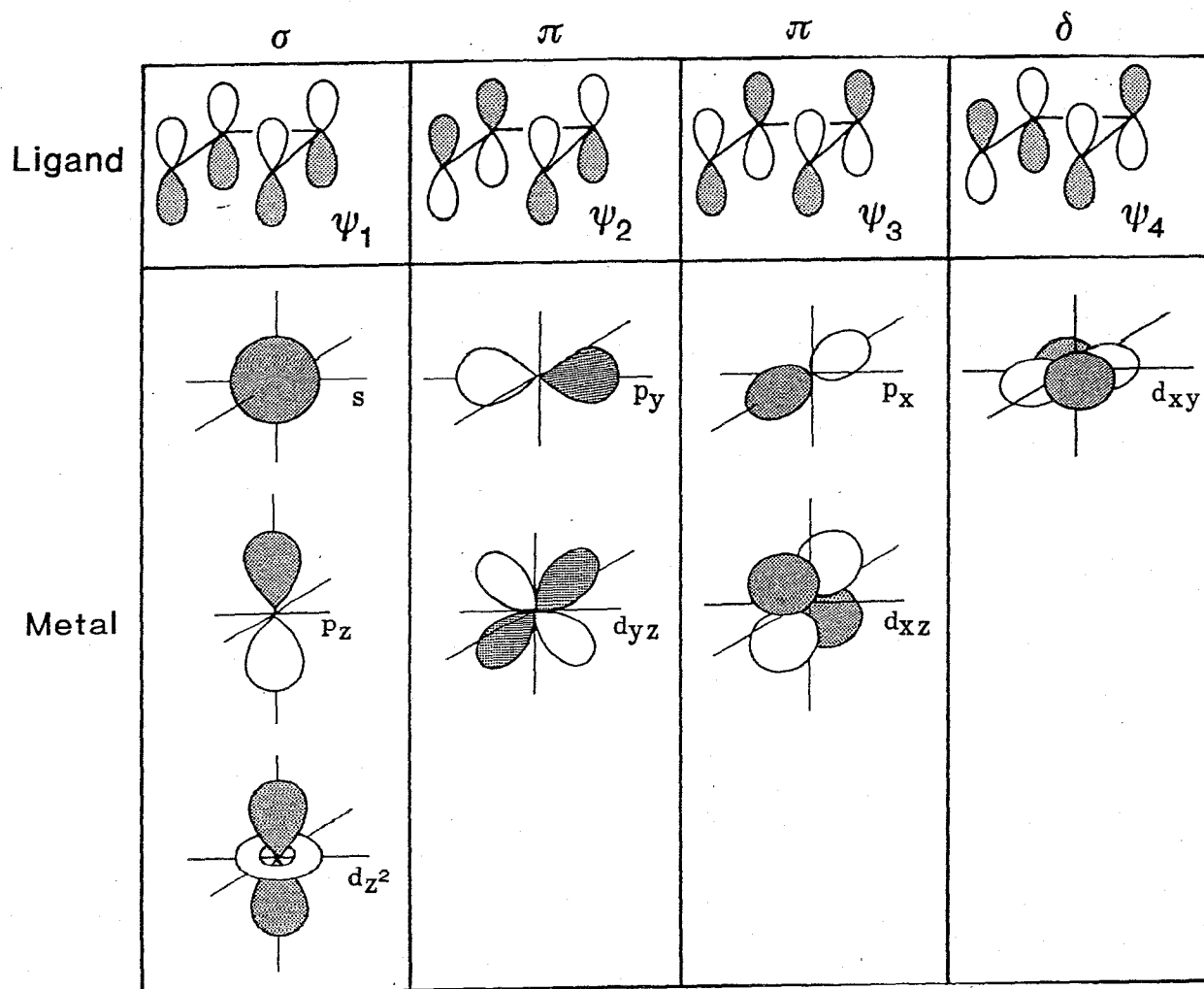
Komplexek π -donor ligandumokkal (6)

A Dewar – Chatt – Duncanson (DCD) modell: $M - C_2$



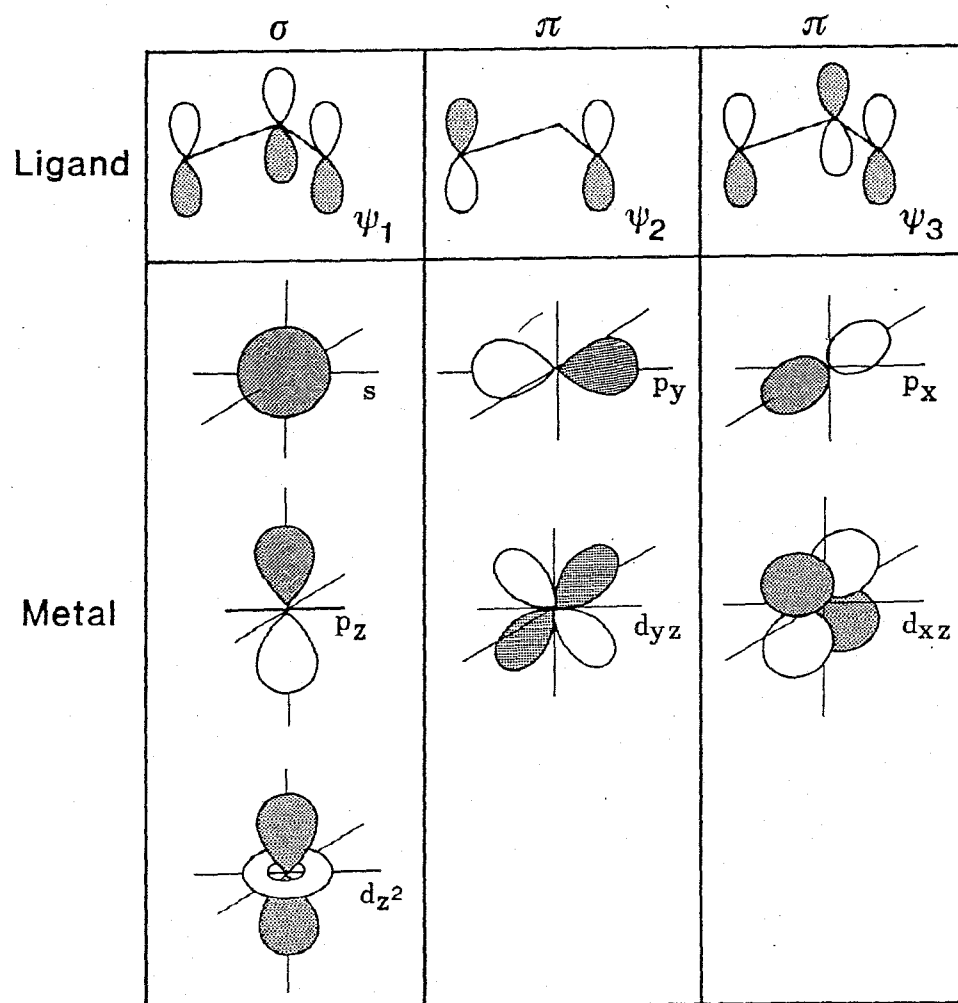
Komplexek π -donor ligandumokkal (7)

A Dewar – Chatt – Duncanson (DCD) modell: M – butadién



Komplexe π -donor ligandumokkal (8)

A Dewar – Chatt – Duncanson (DCD) modell: M – π -allil

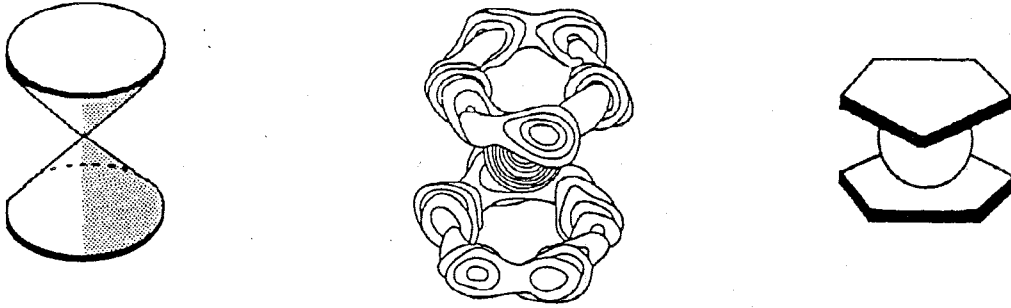


In the ligand $C_3H_5^-$ ψ_1 and ψ_2 are doubly occupied. The metal-ligand bond can be described by the components $\psi_1 \xrightarrow{\sigma} M$, $\psi_2 \xrightarrow{\pi} M$ and $\psi_3 \xleftarrow{\pi} M$. These overlap characteristics induce an electronic rotational barrier within the $(\eta^3\text{-allyl})M$ unit (see p. 287).

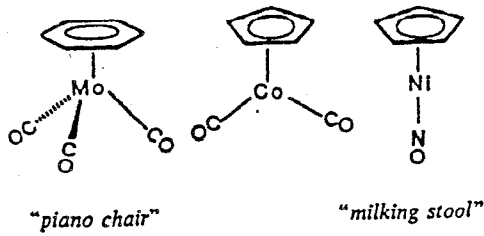
Komplexek π -donor ligandumokkal (9)

Gyűrűs π -donorokkal képzett vegyületek szerkezeti alaptípusai

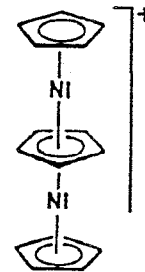
I. „Sandwich” vegyületek



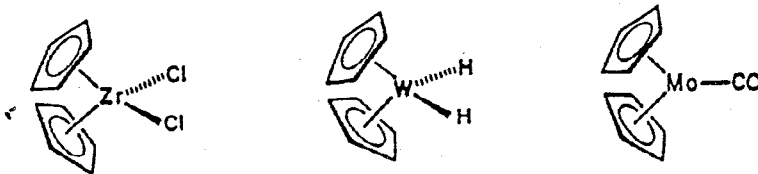
II. Fél-„sandwich” vegyületek



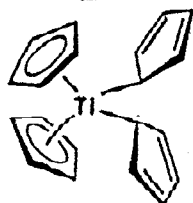
III. Többszörös „sandwich”



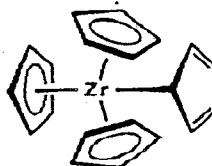
IV. Hajlott „sandwich” vegyületek



V. Vegyületek több, mint két C_5H_5 ligandummal



Cp_2Ti
 $r(Ti^{4+}) = 74 \text{ pm}$
 $(\eta^5-Cp)_2(\eta^1-Cp)_2Ti$



Cp_3Zr
 $r(Zr^{4+}) = 91 \text{ pm}$
 $(\eta^5-Cp)_3(\eta^1-Cp)Zr$

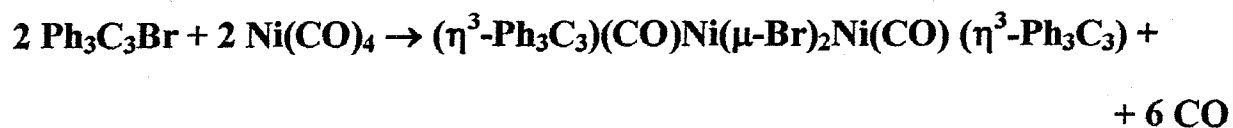


Cp_4U
 $r(U^{4+}) = 117 \text{ pm}$
 $(\eta^5-Cp)_4U$

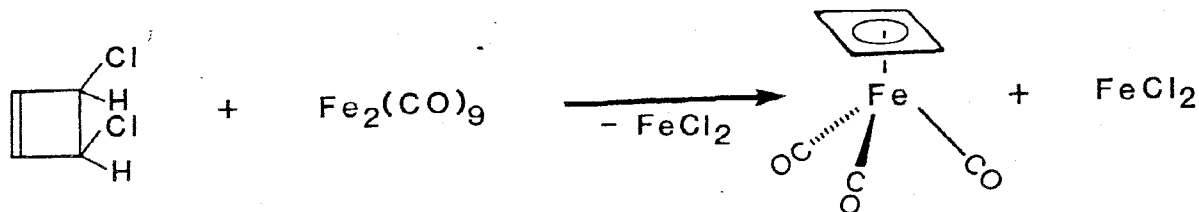
Komplexek π -donor ligandumokkal (10)

Vegyületek (C_nH_n)^{+,0,-} ligandumokkal

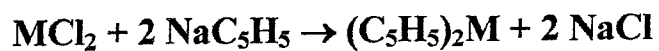
$C_3H_3(+)$ ($C_3Ph_3^+$)



C_4H_4



$C_5H_5(-)$



$M = V, Cr, Mn, Fe,$

Co, Ni

C_6H_6

a) Fischer-Müller reakció (ld. fotokémia);

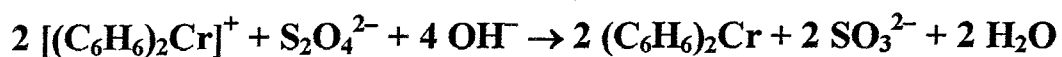
b) CC

c) Fischer-Hafner szintézis

Komplexek π -donor ligandumokkal (11)

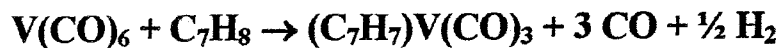
Vegyületek $(C_nH_n)^{+,0,-}$ ligandumokkal (folyt)

C_6H_6 (Fischer-Hafner szintézis)



M = V, Cr, Mo, W, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni

$C_7H_7(+)$



M = V, Mn, Re, Co

$C_8H_8(2-)$



Komplexek π -donor ligandumokkal (12)

A metallocének osztályozása a fém – szén kötéstípus alapján

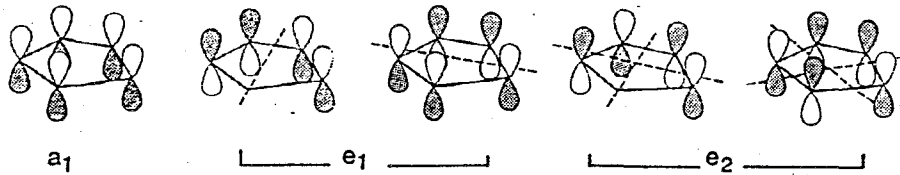
ELECTRONIC STRUCTURE AND BONDING IN THE COMPLEXES $(C_5H_5)_nM$

The properties and bonding types of (cyclopentadienyl)metal compounds can vary over a wide range. In the following table, main-group compounds are also included.

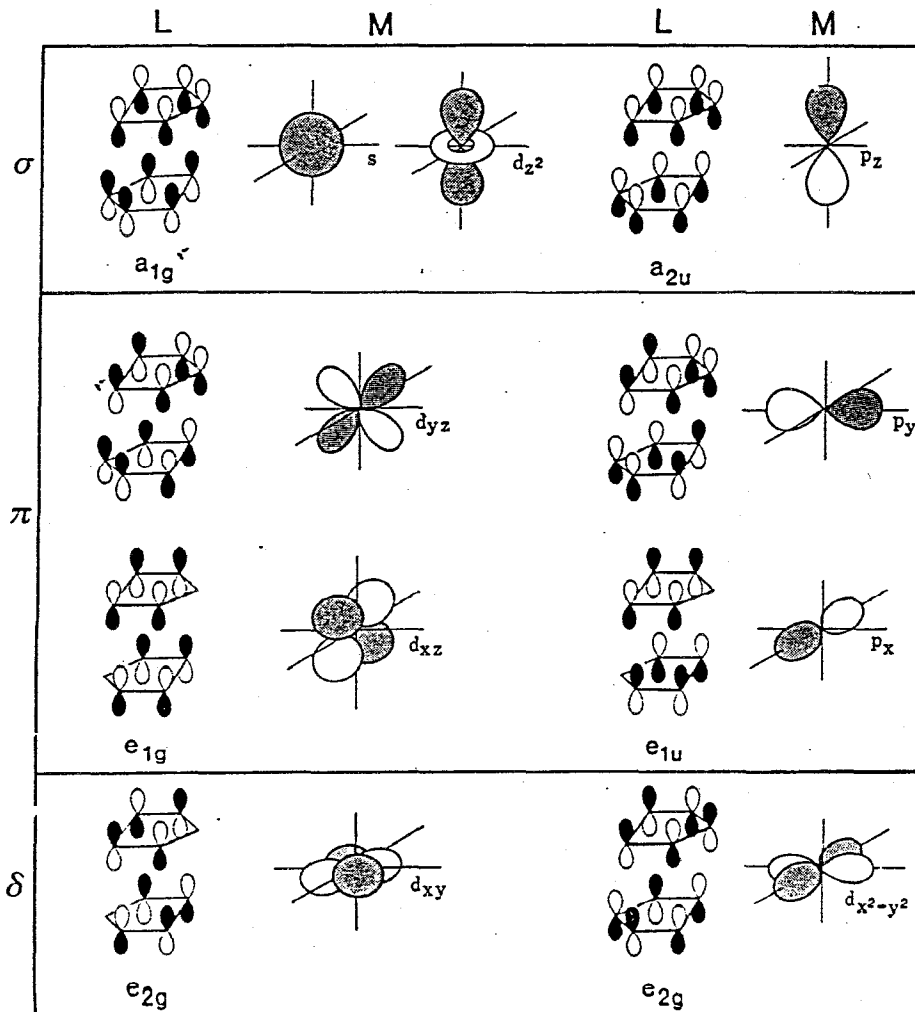
Character	Bonding	Properties	Examples
Ionic	Ionic lattice $M^{n+}[C_5H_5^-]_n$ similar to the halides MX_n	Highly reactive towards air, water and other com- pounds with active hy- drogen, not sublimable	$n = 1$: alkali metals $n = 2$: heavy alkaline earth metals $n = 2, 3$: lanthanoids
Intermediate		Partially sensitive to hydrolysis (exception: TiCp), sublimable	$n = 1$: In, Tl $n = 2$: Be, Mg, Sn, Pb, Mn, Zn, Cd, Hg
Covalent	molecular lattice π -MO(C_5H_5) ↓ M(<i>s, p, d</i>) and π^* -MO(C_5H_5) ↑ M(<i>d</i>)	Only partially air-sensi- tive, in general stable to hydrolysis, sublimable	$n = 2$: (Ti), V, Cr, (Re), Fe, Co, Ni, Ru, Os, (Rh), (Ir) $n = 3$: Ti $n = 4$: Ti, Zr, Nb, Ta, Mo, U, Th

Komplexek π -donor ligandumokkal (13)

A Fe - Cp kötés (ferrocén)

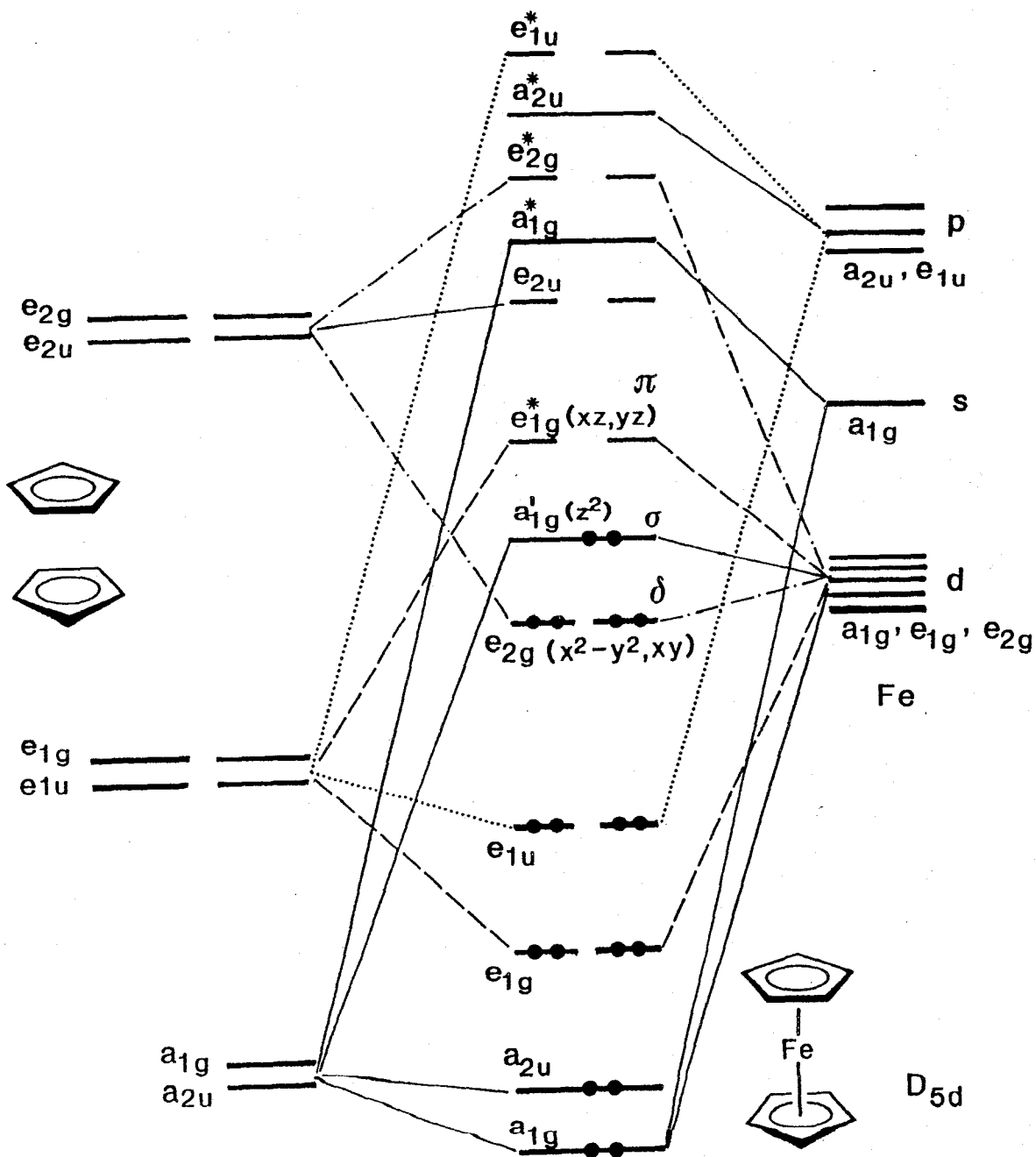


These ligand π orbitals are united pairwise, using plus and minus signs, to form symmetry-adapted linear combinations (SALC) which then overlap with metal orbitals of appropriate symmetry. For a metallocene in its staggered conformation (D_{5d}) the following interactions result:



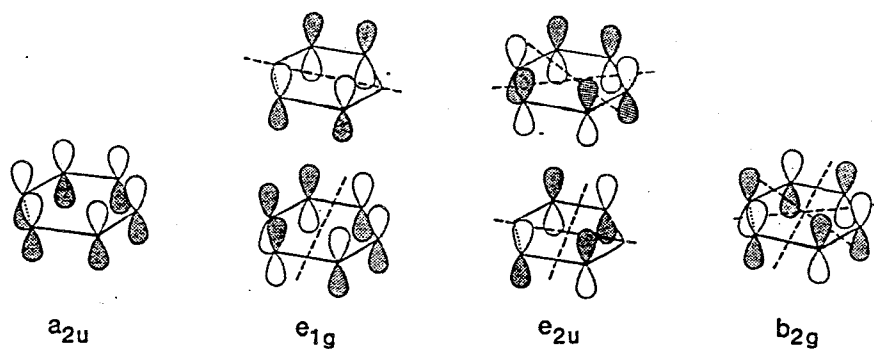
Komplexek π -donor ligandumokkal (14)

A ferrocén molekulapályái (18 VE)

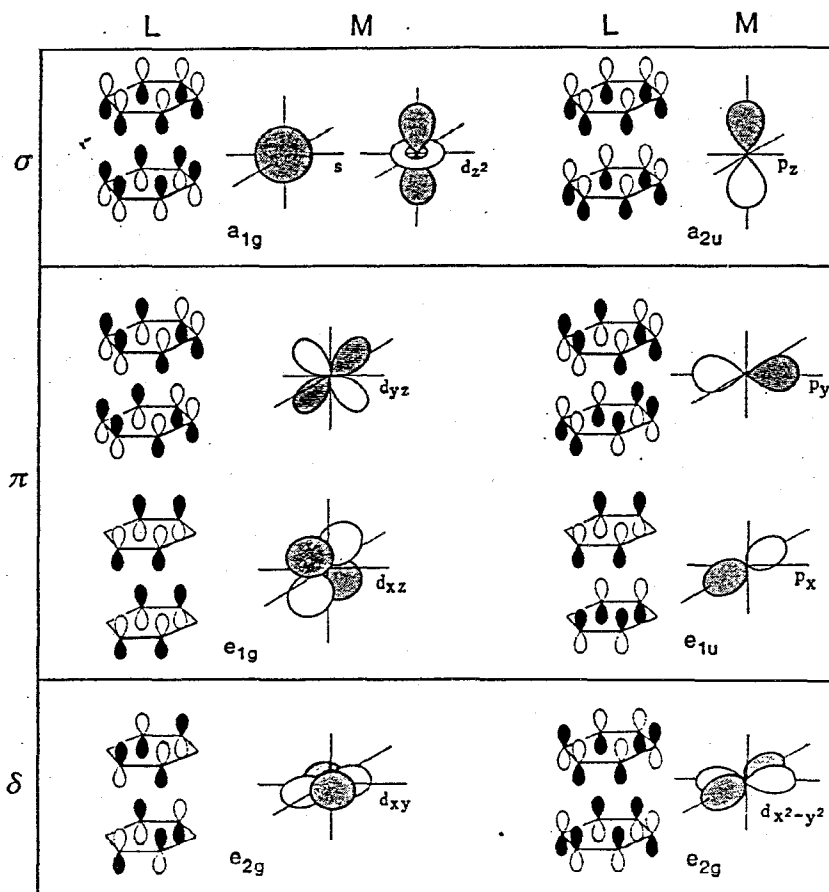


Komplexek π -donor ligandumokkal (15)

A Cr - C₆H₆ kötés

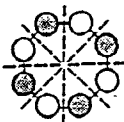
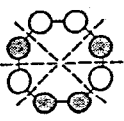
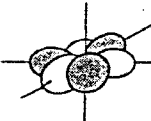
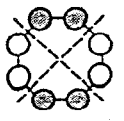
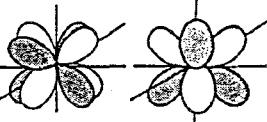
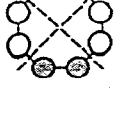
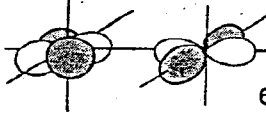
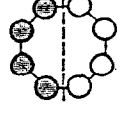
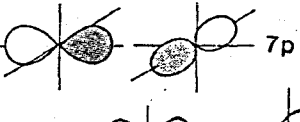
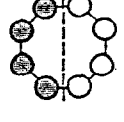
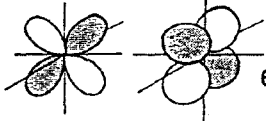
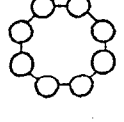

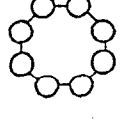
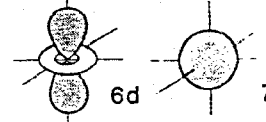


Interactions of symmetry-adapted linear combinations of the π MO's of two C₆H₆ ligands with appropriate metal orbitals in bis(benzene)chromium (D_{6h}):

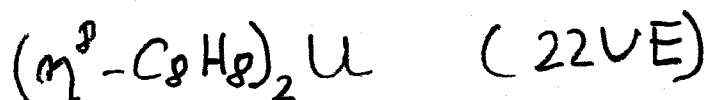


Komplexek π -donor ligandumokkal (16)

Az U – C_8H_8 kötés

	$C_8H_8^{2-}$	$C_8H_8^{2-}$	Metal-AO		Metal- C_8H_8
Occupation	Symmetry*	SALC	Metal AO's with the same symmetry as the SALC		Bond type
—	b_{2u} 		—		
==	e_{3g} 	e_{3u}	 5f		φ
	e_{2u} 	e_{2u}	 5f		δ
•••	e_{2u} 	e_{2g}	 6d		δ
•••	e_{1g} 	e_{1u}	 7p		π
•••	e_{1g} 	e_{1g}	 6d		π
•••	a_{2u} 	a_{2u}	 7p		σ
•••	a_{2u} 	a_{1g}	 6d 7s		σ

* For the sake of clarity, ligand MO's are shown from above. Their phases invert in the plane of the paper (= nodal plane).



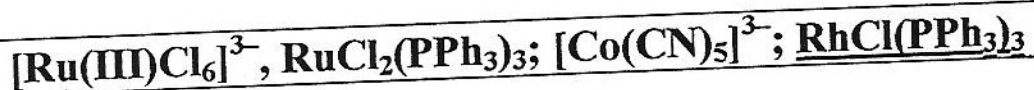
Homogén katalízis (1)

Szerves átmenetifém komplexek tipikus reakciói

Reakció	ΔVE	ΔOSz	ΔKsz	Példa
Lewis sav disszociáció	0	0	-1	$Cp_2WH_2 * BF_3 \leftrightarrow BF_3 + Cp_2WH_2$
Lewis sav asszociáció	0	0	+1	
Lewis bázis disszociáció	-2	0	-1	$Pt(PPh_3)_4 \leftrightarrow PPh_3 + Pt(PPh_3)_3$
Lewis bázis asszociáció	+2	0	+1	
Reduktív elimináció	-2	-2	-2	$H_2Ir^{III}Cl(CO)L_2 \leftrightarrow H_2 + Ir^I Cl(CO)L_2$
Oxidatív addíció	+2	+2	+2	
Beékelődés	-2	0	-1	$MeMn(CO)_5 \leftrightarrow MeCOMn(CO)_4$
Kilökődés	+2	0	+1	
Oxidatív gyűrűzárás	-2	+2	0	$(\pi-C_2F_4)_2Fe^0(CO)_3 \leftrightarrow (CF_2)_4Fe^II(CO)_3$
Reduktív gyűrűhasadás	+2	-2	0	

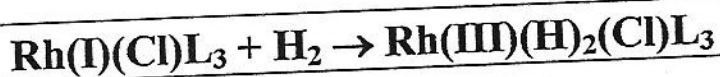
Homogén katalízis (2)

OLEFINEK HIDROGÉNEZÉSE

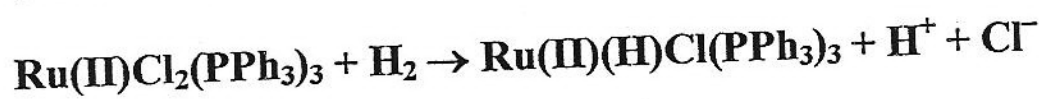


Bevezető lépés

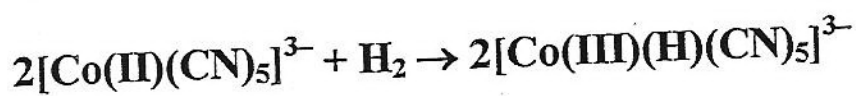
a) Oxidatív addíció (dihidrid köztitermék)



b) Heterolitikus hasítás (monohidrid köztitermék)

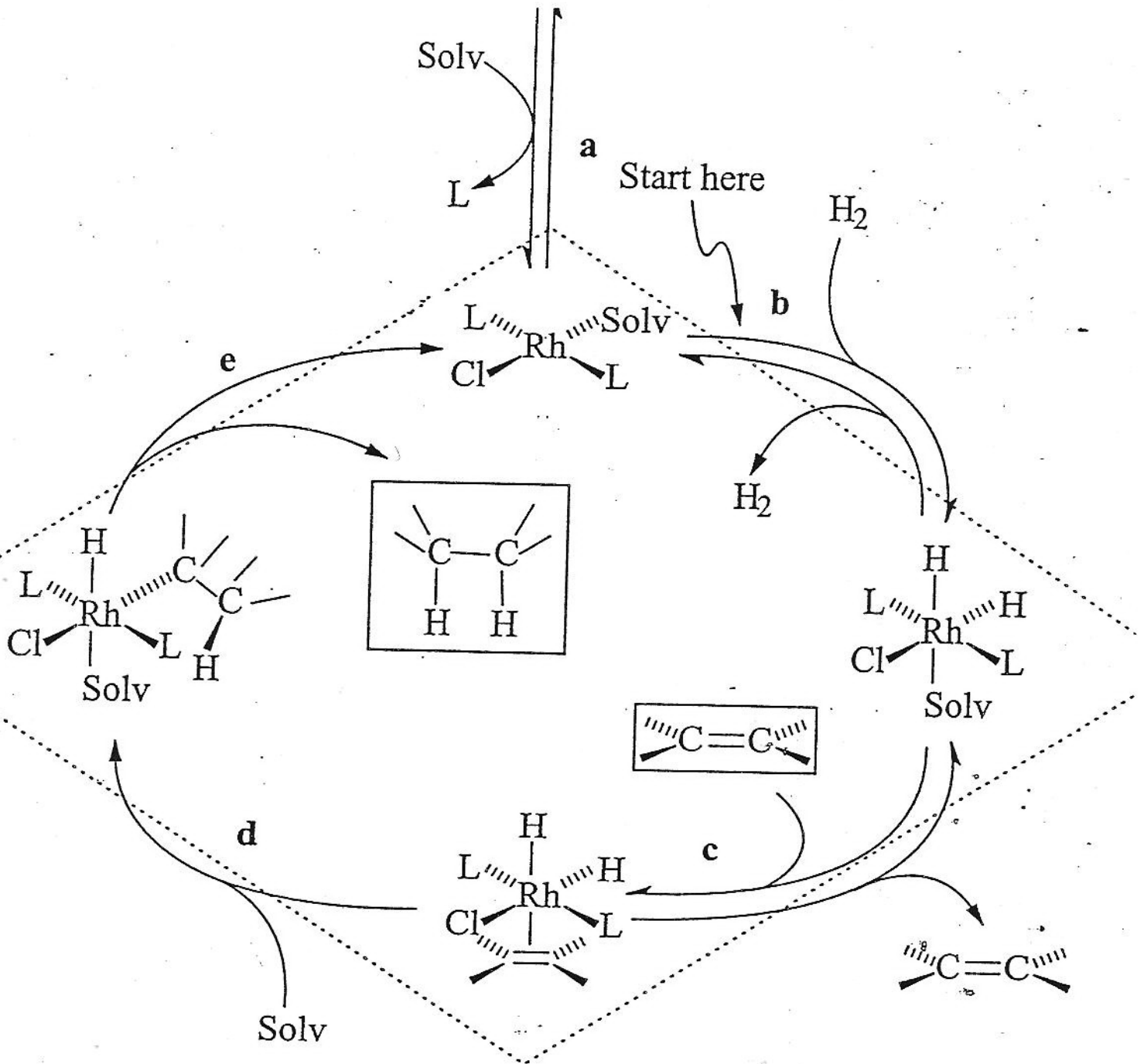


c) Homolitikus hasítás (monohidrid köztitermék)



Homogén katalízis (3)

Alkének hidrogénezése (Wilkinson)



Key Steps: a, b, c, d, e

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Homogén katalízis (4)

Az etén oxidációja (Wacker-f. szint)

