

ΒΙΒΛΙΟΓΡΑΦΙΑ

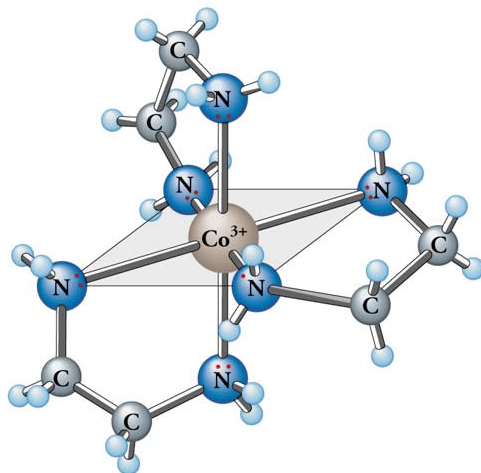
Multiple Bonds Between Metal Atoms, Eds F. A. Cotton, C. A. Murillo, R. A. Walton, third edition, Springer Science and Business Media

Metal-Metal Bonding, Ed G. Parkin, *Structure and Bonding*, Volume 136, 2010

Metal Clusters in Chemistry, Eds P. Braunstein, L. A. Oro, P. R. Raithby, Wiley VCH

Werner (Coordination Chemistry)

...the compounds he dealt with were regarded (and correctly so) as simply the result of conjoining two or more mononuclear complexes through shared ligand atoms...



...properties of these complexes were accounted for entirely in terms of the various *individual metal atoms and the local sets of metal-ligand bonds*. No direct M–M interactions of any type were considered and the concept of a metal-metal bond remained wholly outside the scope of *Wernerian chemistry*, even in polynuclear complexes

“Strange compounds”....not compatible with Werner ‘s theory

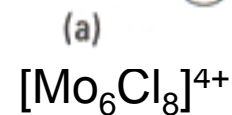
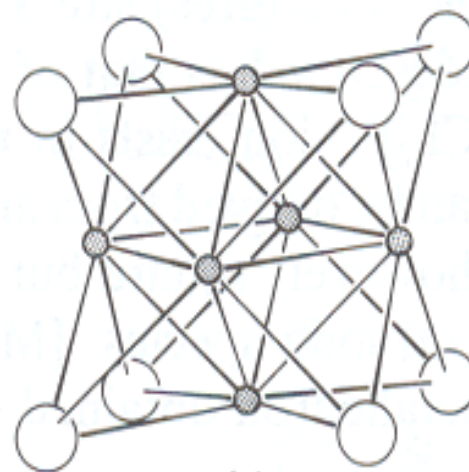
1736 F. Peligant



1857-1861 Christian Wilhelm Blomstrand

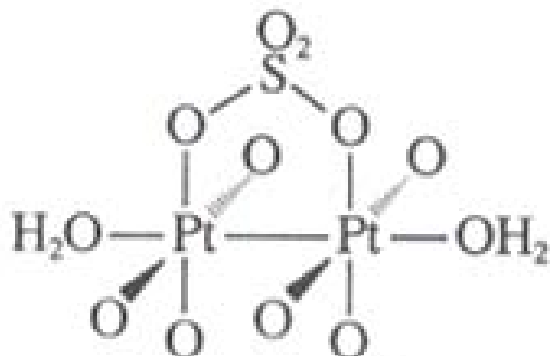
Ένωση Mo^{II} με Cl με αναλογία $\text{Mo}:\text{Cl} < 1:2 \dots ???$

...μόνο το $1/3$ του Cl^- καταβυθιζόταν με Ag^+

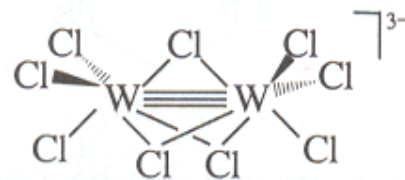


...more “Strange compounds”....

1905 Blondel



1907 Olsen



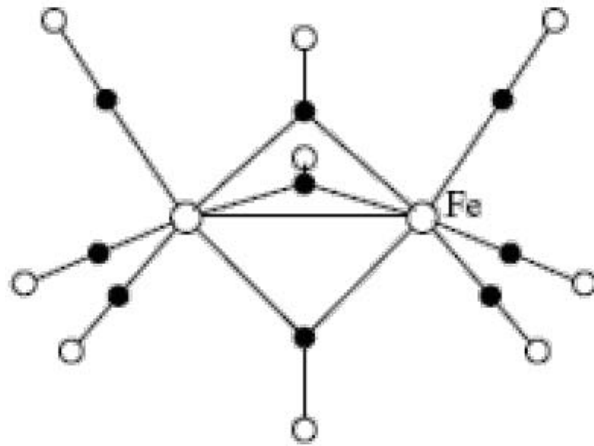
1934 Brossen

Face-Sharing Bioctahedra: (δύο οκτάεδρα που διαμοιράζονται μια έδρα)
FSBO

ΙΣΤΟΡΙΚΗ ΑΝΑΔΡΟΜΗ

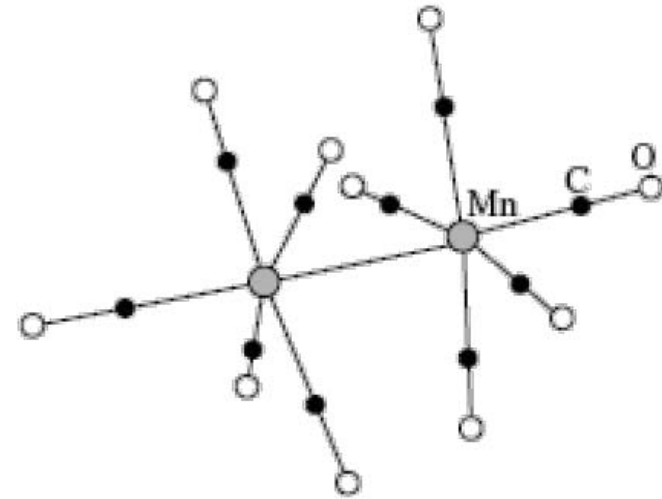
1939

$\text{Fe}_2(\text{CO})_9$
Απλός δεσμός Fe-Fe $\sim 2.5\text{\AA}$

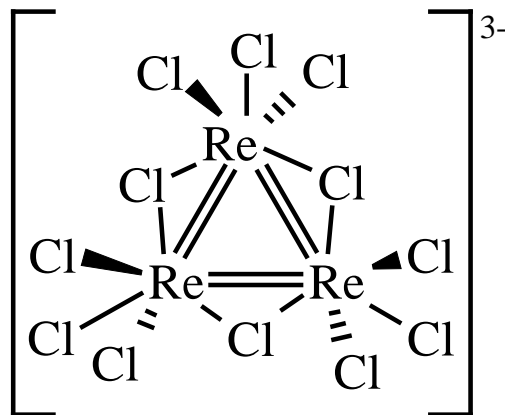
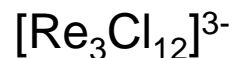


1957

$\text{Mn}_2(\text{CO})_{10}$
Δεν υπάρχουν γέφυρες CO



1963



Benzene analogue....Re=Re bond was assumed but could not be proved, at least not yet

(a) F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.* **1964**, 233.

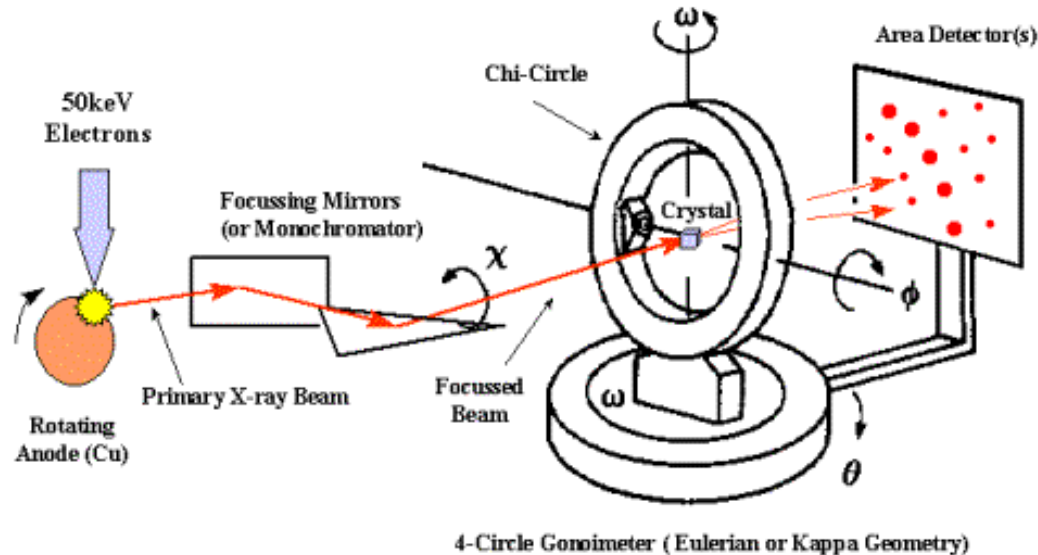
(b) *idem.*, *Inorg. Chem.* **1964**, 3, 1402;

(c) F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.* **1964**, 86, 4497;

(d) F. A. Cotton, S. J. Lippard and J. T. Mague, *Inorg. Chem.* **1965**, 4, 508;

(e) J. Gelinek and W. Rudorff, *Naturwiss.* **1964**, 51, 85.

How did it all begun?....1950s: X-ray's in the house...



C. Brosset. *Arkiv Kemi, Miner. Geol.* **1946**, A20 (7); A22 (11).

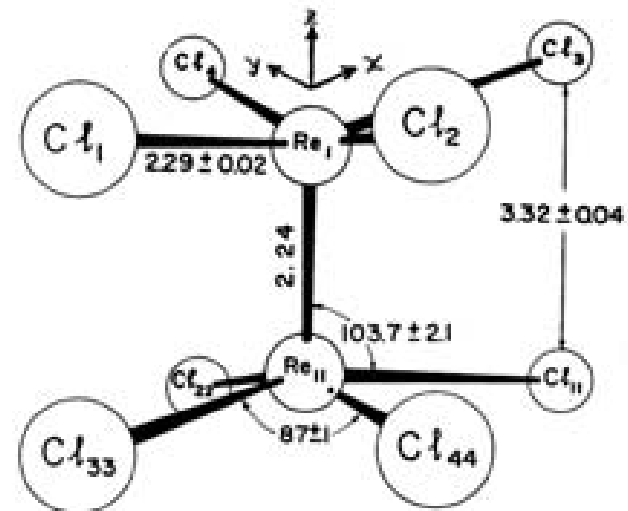
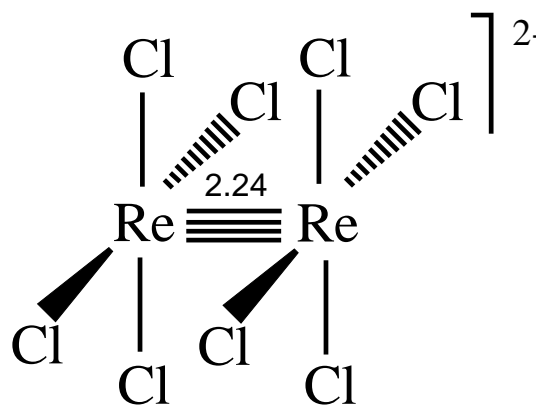
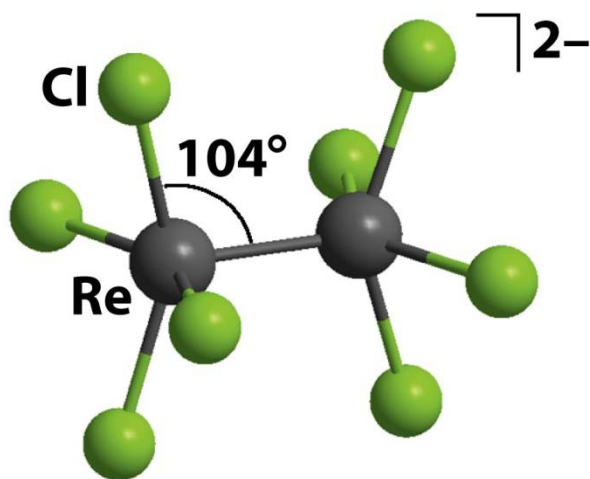
...the lower chlorides of **Mo** contain octahedral groups of metal atoms with Mo–Mo distances **even shorter (~2.6 Å) than those in metallic molybdenum (2.725 Å)**....but no further research activity...

1950: an X-ray diffraction experiment, albeit of an unconventional type carried out on aqueous solutions, showed that $\text{Ta}_6\text{Cl}_{14}\cdot 7\text{H}_2\text{O}$ and its bromide analog, as well as the corresponding **niobium** compounds, also contain octahedral groups of metal atoms with rather short M–M distances ($\sim 2.8 \text{ \AA}$).

...but again these remarkable observations did not lead to any further exploration of such chemistry...

...big bang theory...

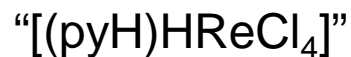
1964



Cotton et al...during attempts to prepare and study $[\text{Re}_3\text{Cl}_{12}]^{3-}$

...”first evidence” V. G. Tronev and S. M. Bondin, *Khim. Redk. Elem. Akad. Nauk SSSR* **1954**, 1, 40

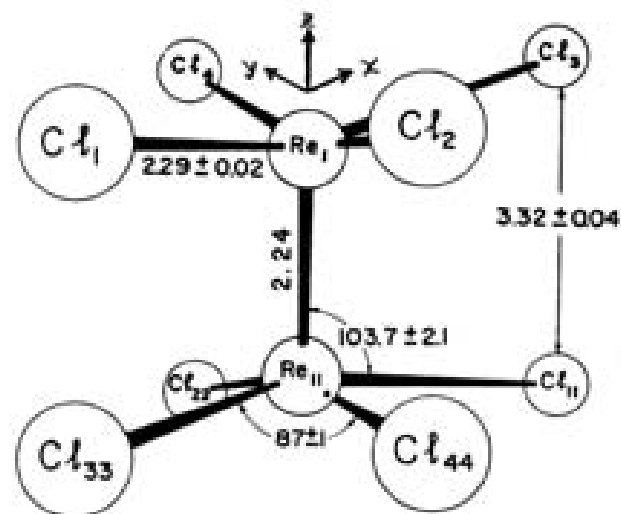
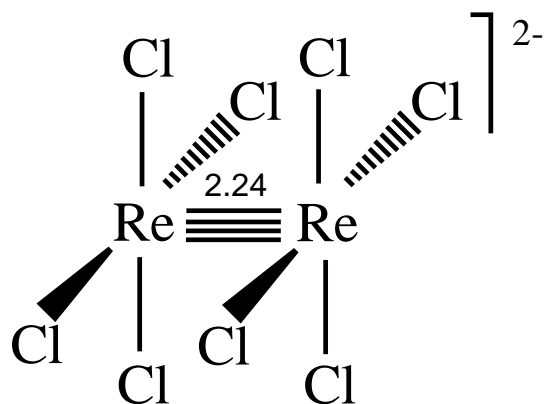
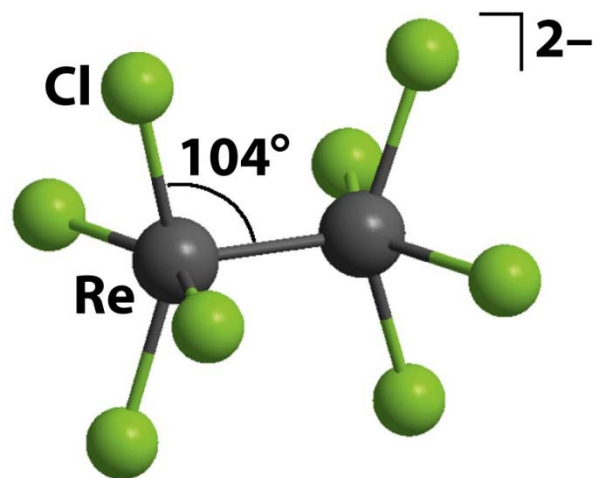
Eight chlorine atoms constitute a square prism with two rhenium atoms lying within the prism, whereby each rhenium atom is surrounded by four neighboring chlorine atoms situated at the apices of a strongly flattened tetragonal pyramid. The apices of two such pyramids approach each other generating the prism. **In such a structure, each rhenium atom has for its neighbors one rhenium atom, at a distance of 2.22 Å** and four chlorine atoms at a distance of 2.43 Å. As a result, the dimeric ion $[\text{Re}_2\text{Cl}_8]^{4-}$ is generated.



V. G. Kuznetsov and P. A. Koz'min, *J. Struct. Chem.* **1963**, 4, 49.

...but it was not very correct structure... since there had been, according to the experimental section of the paper, severe difficulty with crystal twinning.

F. A. Cotton and C. B. Harris, *Inorg. Chem.* **1965**, 4, 330.



F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. S. Wood, *Science* **1964**, 145, 1305.

“...the charge on the Re_2Cl_8 unit was indeed $2-$ and not $4-$, as believed by the Soviet workers”

ΤΑΞΕΙΣ ΔΕΣΜΩΝ

ΑΝΤΙΔΡΑΣΕΙΣ ΣΥΣΤΗΜΑΤΩΝ ΜΕ Μ-Μ

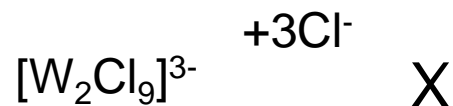
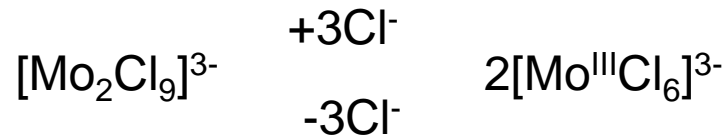
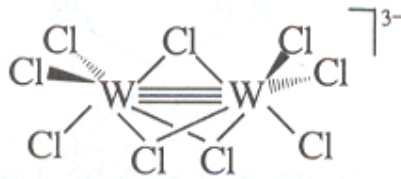
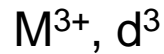
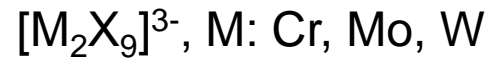
Οξειδοαναγωγικές αντιδράσεις

Ενεργοποίηση υποστρωμάτων

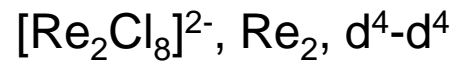
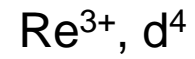


ΔΕΣΜΟΙ M-M

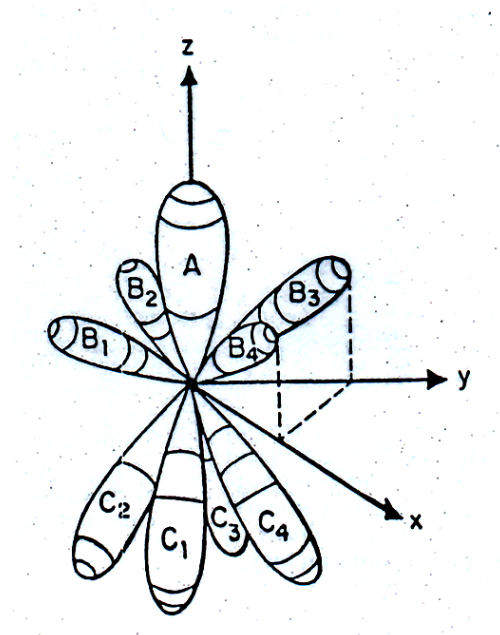
Μέγεθος, σθένος ιόντων, σταθεροποίηση κρυσταλλικού πεδίου, ύπαρξη δεσμού M-M καθορίζουν τη χημική δραστηριότητα και τη δομή των στοιχείων μετάπτωσης



ΔΕΣΜΟΙ M-M

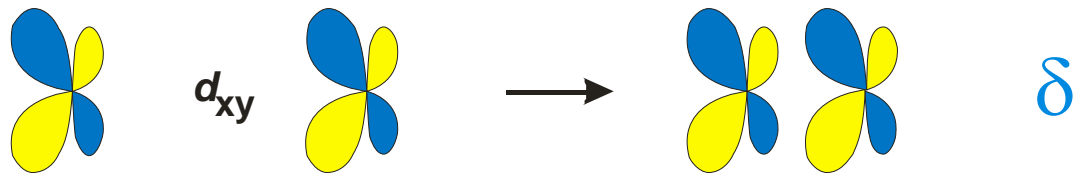
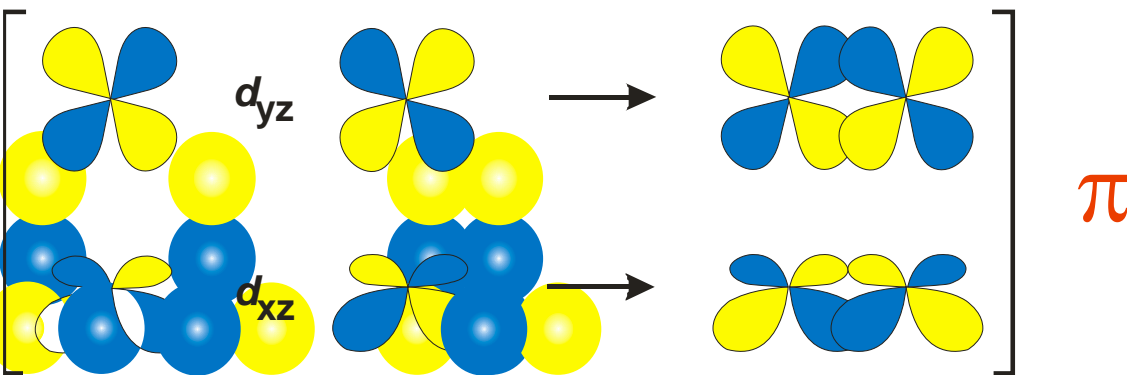


Πρώτη προσέγγιση: d^5sp^3 υβριδικά τροχιακά $5 + 1 + 4 = 9$



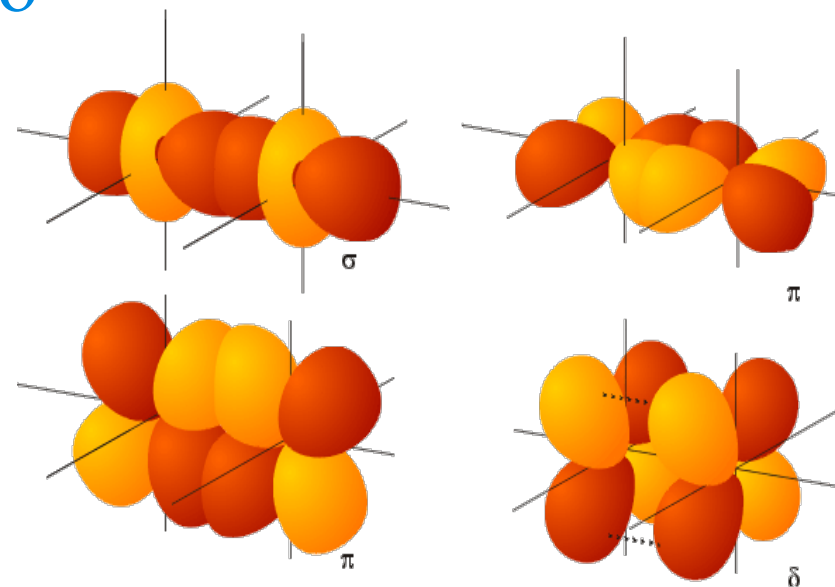
ΔΕΣΜΟΙ M-M

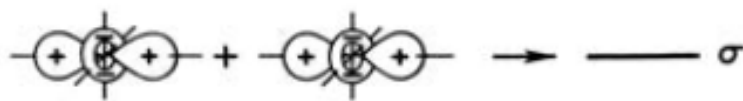
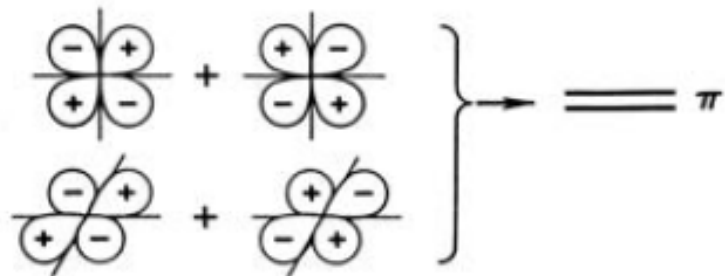
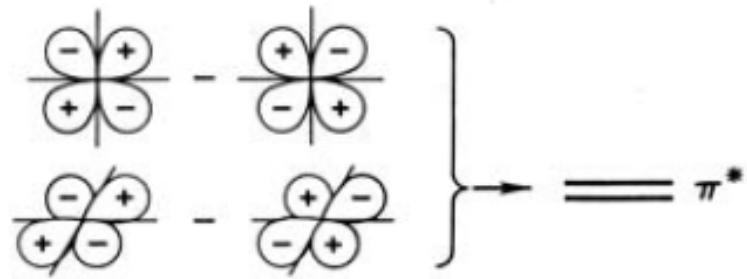
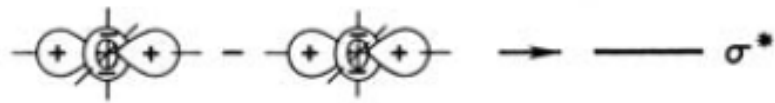
p_z is also present in here...



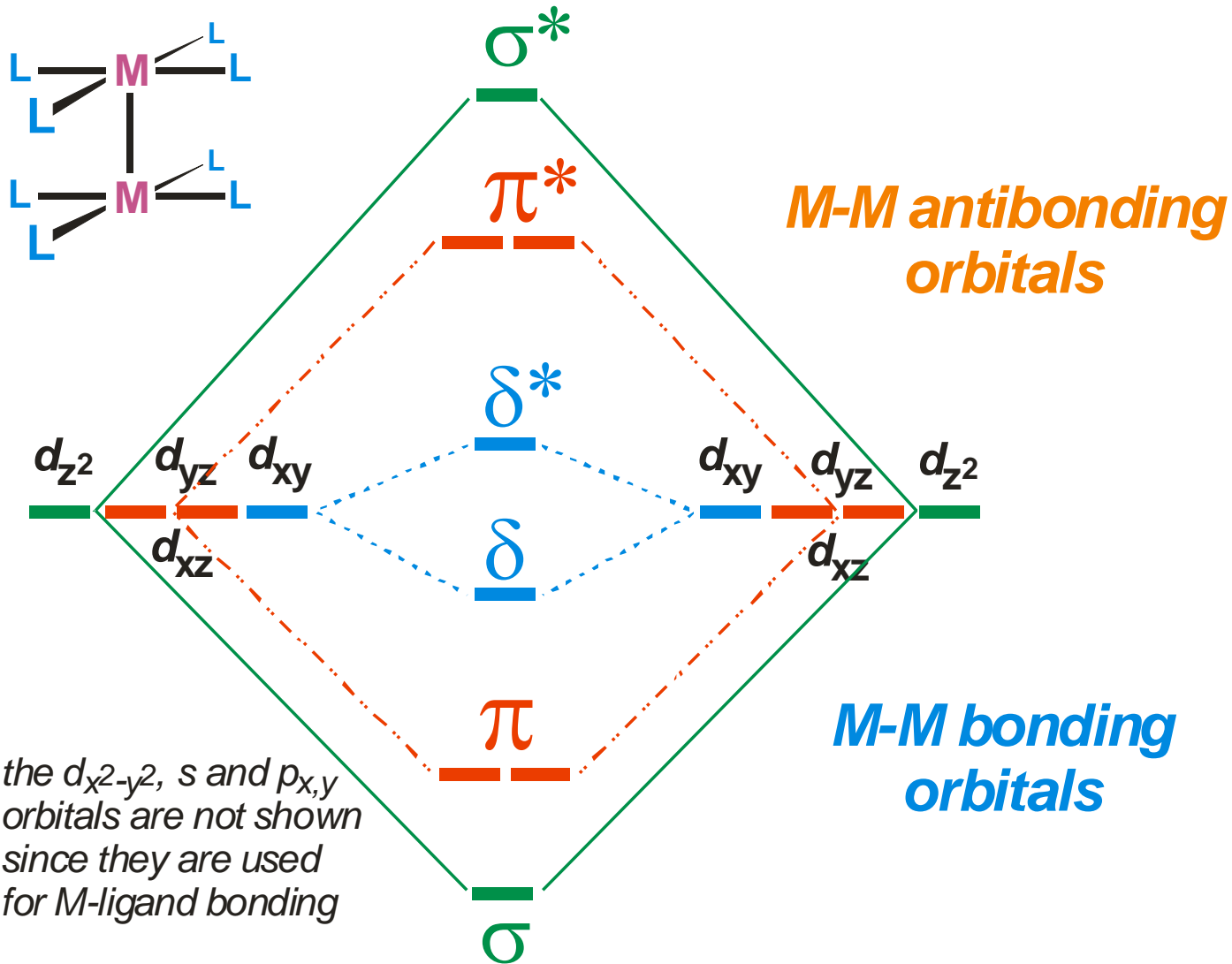
the $d_{x^2-y^2}$ orbitals (not shown) are used for M-L bonding

$$\begin{aligned} &\sigma(d_{z^2} - d_{z^2}) \\ &\pi(d_{xz} - d_{xz}) \\ &\pi(d_{yz} - d_{yz}) \\ &\delta(d_{xy} - d_{xy}) \end{aligned}$$

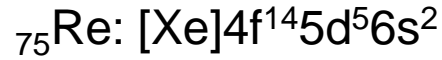




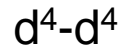
ΔΕΣΜΟΙ M-M



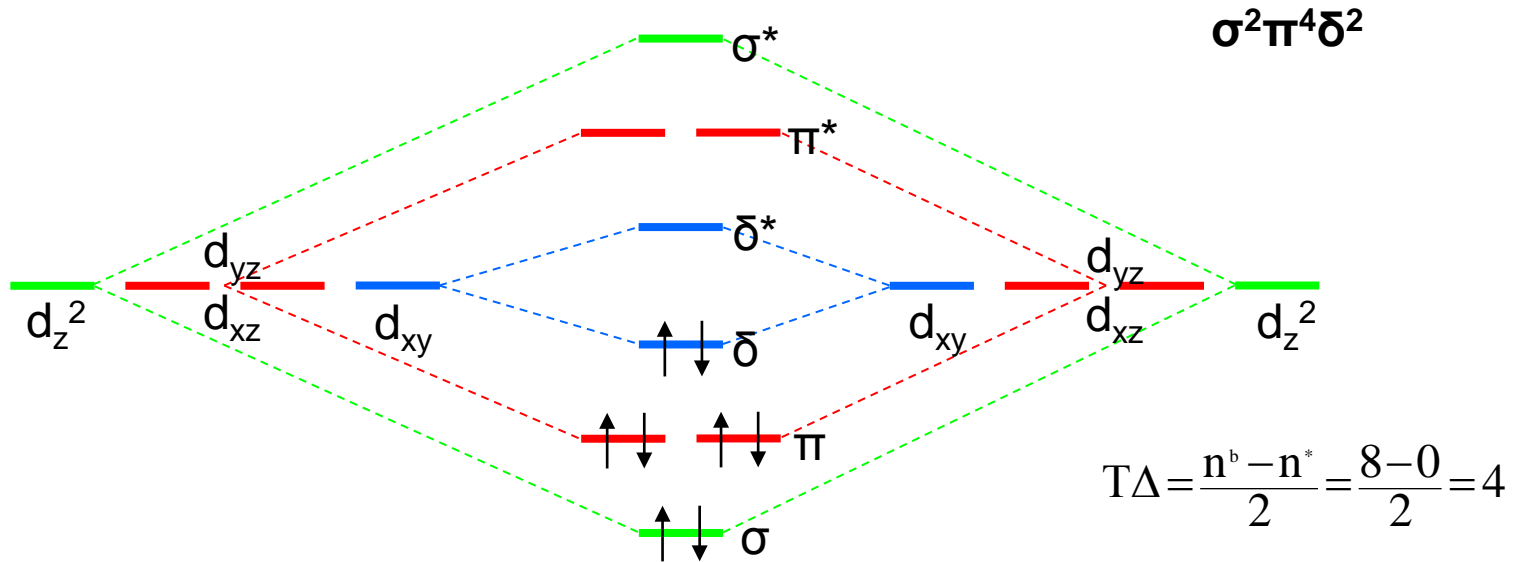
ΔΕΣΜΟΙ M-M



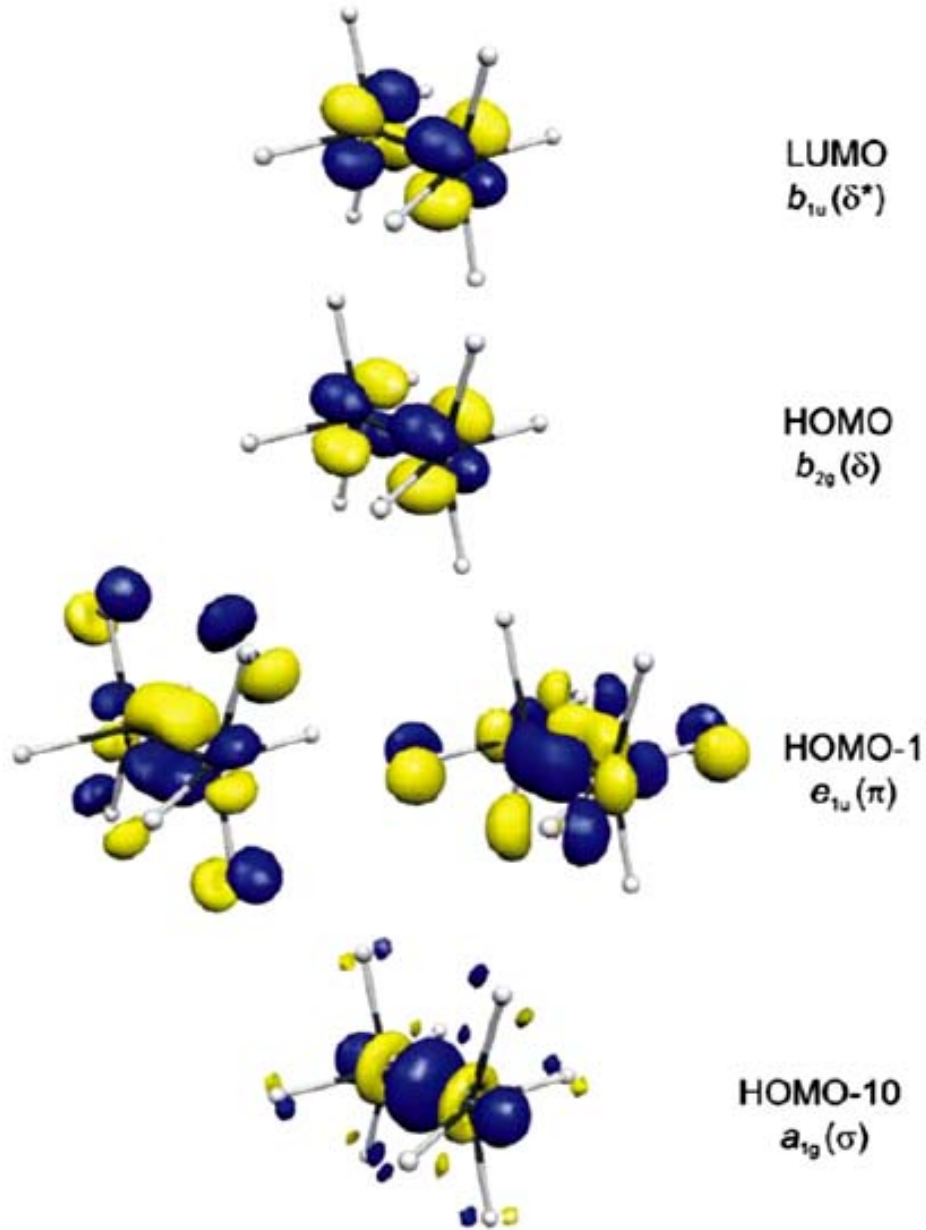
$$\text{Re}^{n+}: 2x + 8(-1) = -2 \Rightarrow 2x = +6 \Rightarrow x = +3$$



8e⁻ στο διάγραμμα των MO

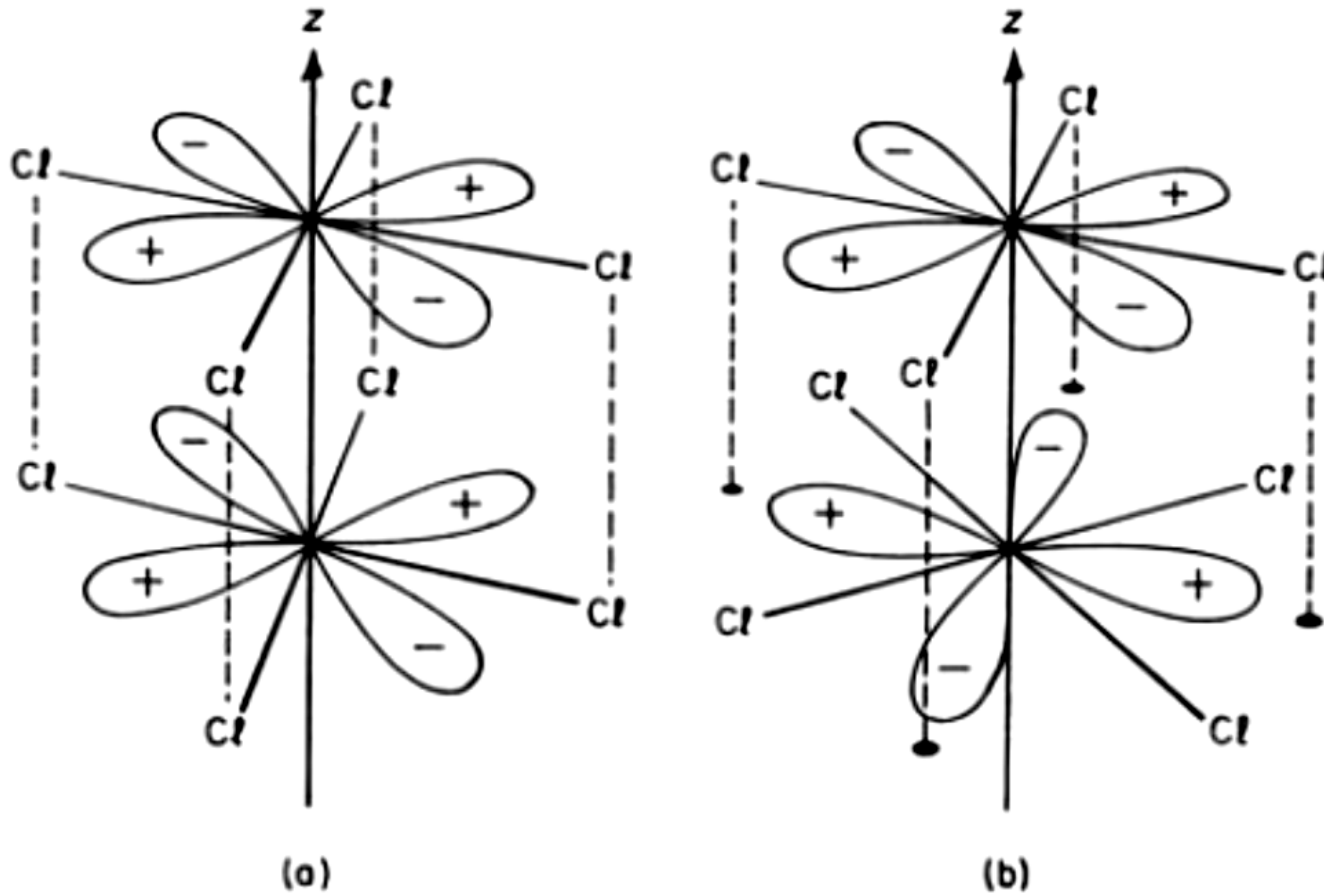


ΔΕΣΜΟΙ M-M



Διάγραμμα του κενού
LUMO και των
κατειλημμένων τροχιακών
σθένους του $[\text{Re}_2\text{Cl}_8]^{2-}$
 $\sigma^2\pi^4\delta^2$

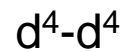
ΔΕΣΜΟΙ M-M



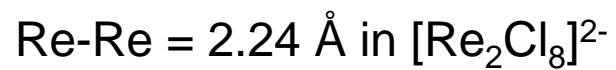
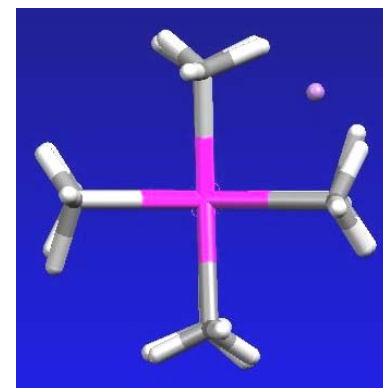
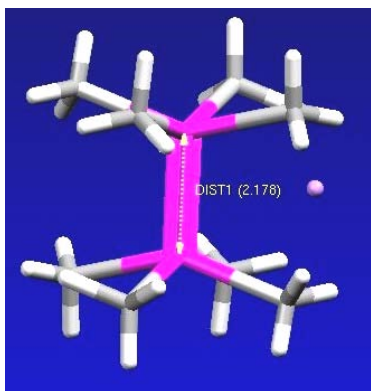
(a) εκλειπτική (eclipsed) και (b) διαβαθμισμένη (staggered) διαμόρφωση

Τι διαμόρφωση περιμένουμε για το $[\text{Re}_2\text{Cl}_8]^{2-}$

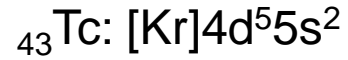
ΔΕΣΜΟΙ M-M



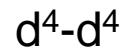
$$T\Delta = \frac{n^b - n^*}{2} = \frac{8 - 0}{2} = 4$$



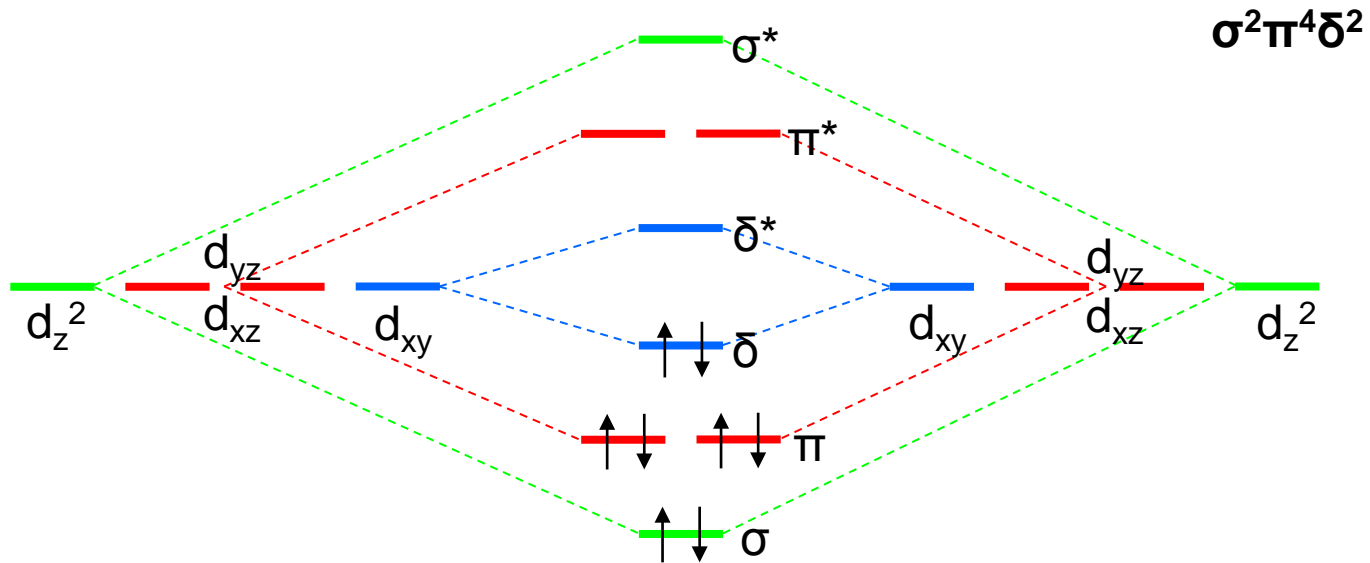
ΔΕΣΜΟΙ M-M



$$\text{Tc}^{n+}: 2x + 8(-1) = -2 \Rightarrow 2x = +6 \Rightarrow x = +3$$



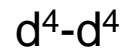
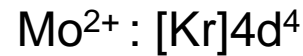
8e⁻ στο διάγραμμα των MO



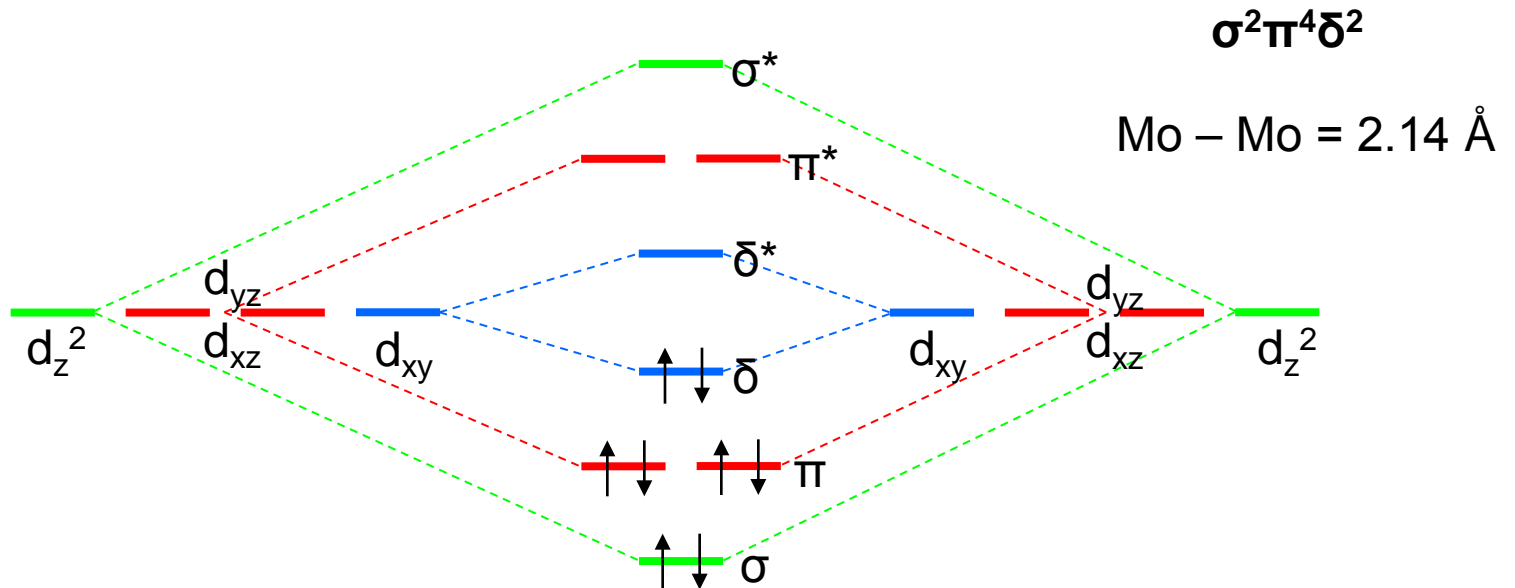
ΔΕΣΜΟΙ M-M



$$\text{Mo}^{n+}: 2x + 8(-1) = -4 \Rightarrow 2x = +4 \Rightarrow x = +2$$



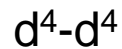
8e⁻ στο διάγραμμα των MO



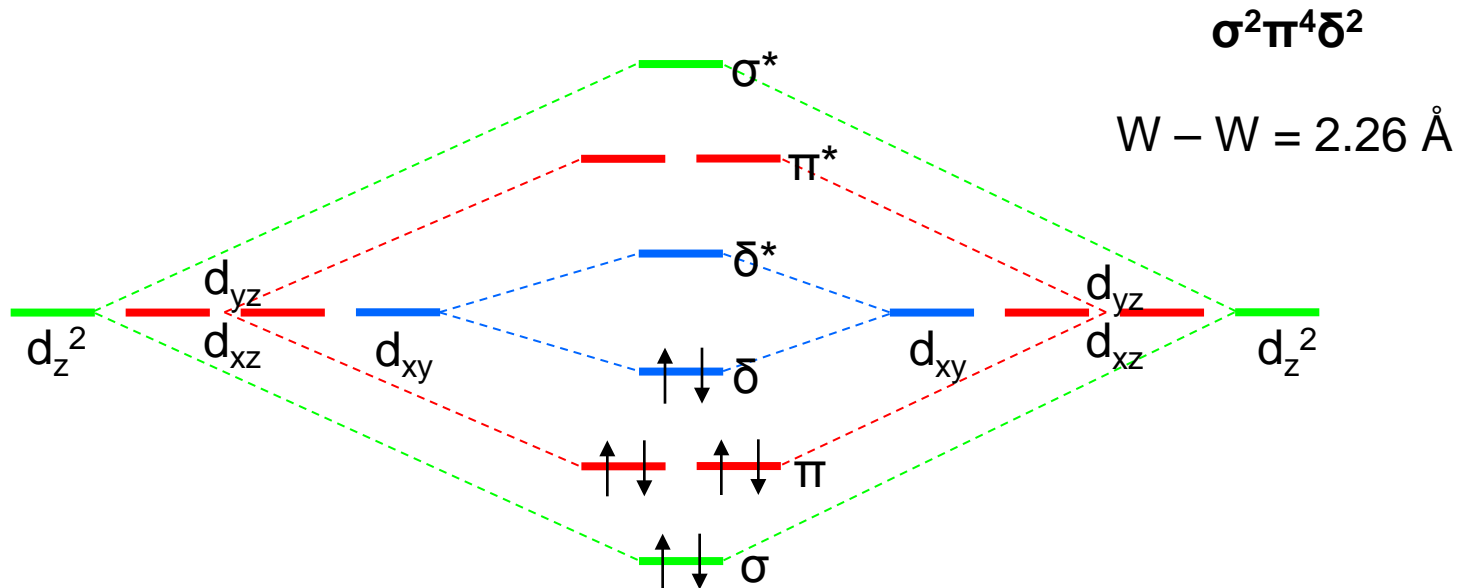
ΔΕΣΜΟΙ M-M



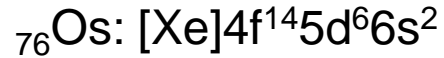
$$W^{n+}: 2x + 8(-1) = -4 \Rightarrow 2x = +4 \Rightarrow x = +2$$



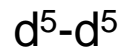
8e⁻ στο διάγραμμα των MO



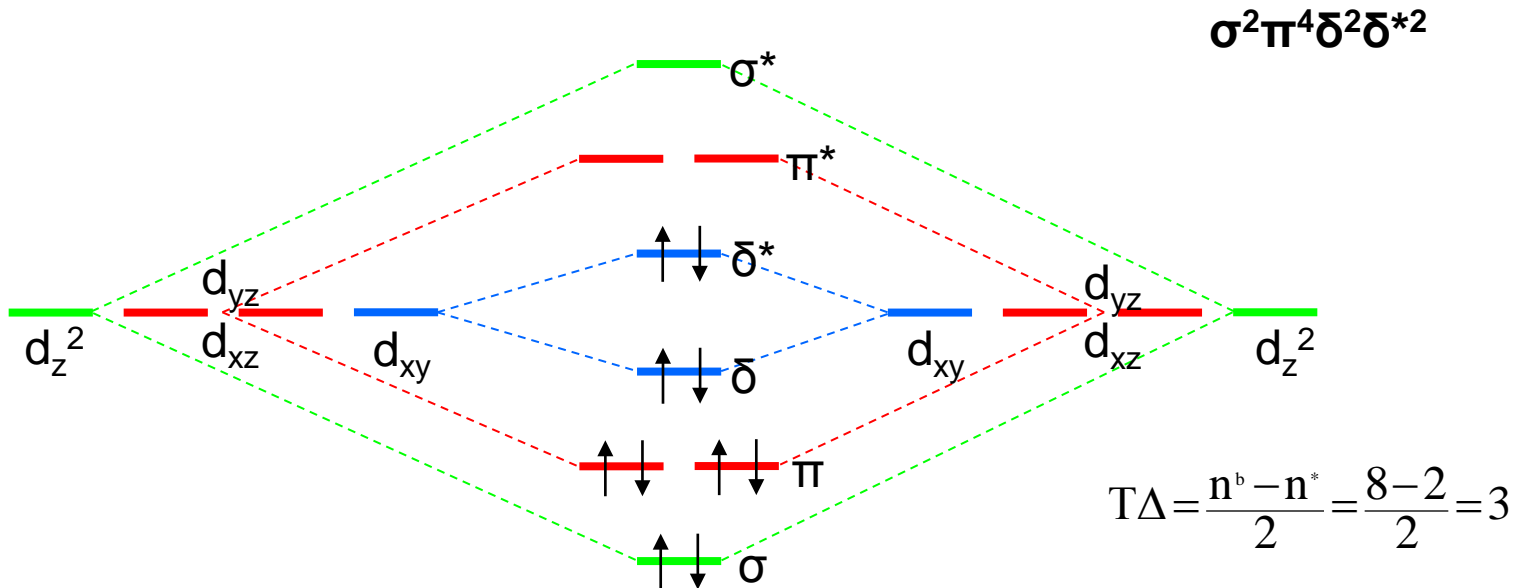
ΔΕΣΜΟΙ M-M



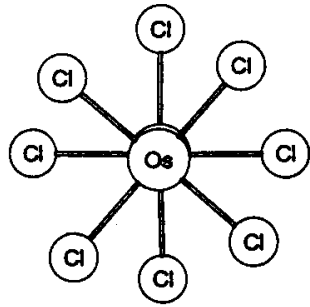
$\text{Os}^{n+}: 2x + 8(-1) = -2 \Rightarrow 2x = +6 \Rightarrow x = +3$



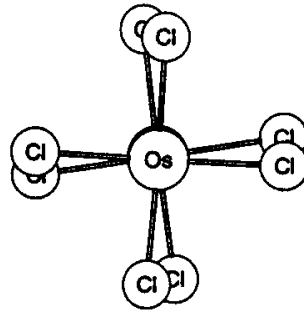
10e⁻ στο διάγραμμα των MO



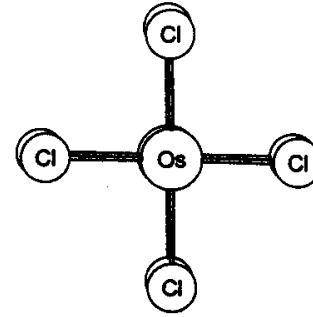
ΔΕΣΜΟΙ M-M



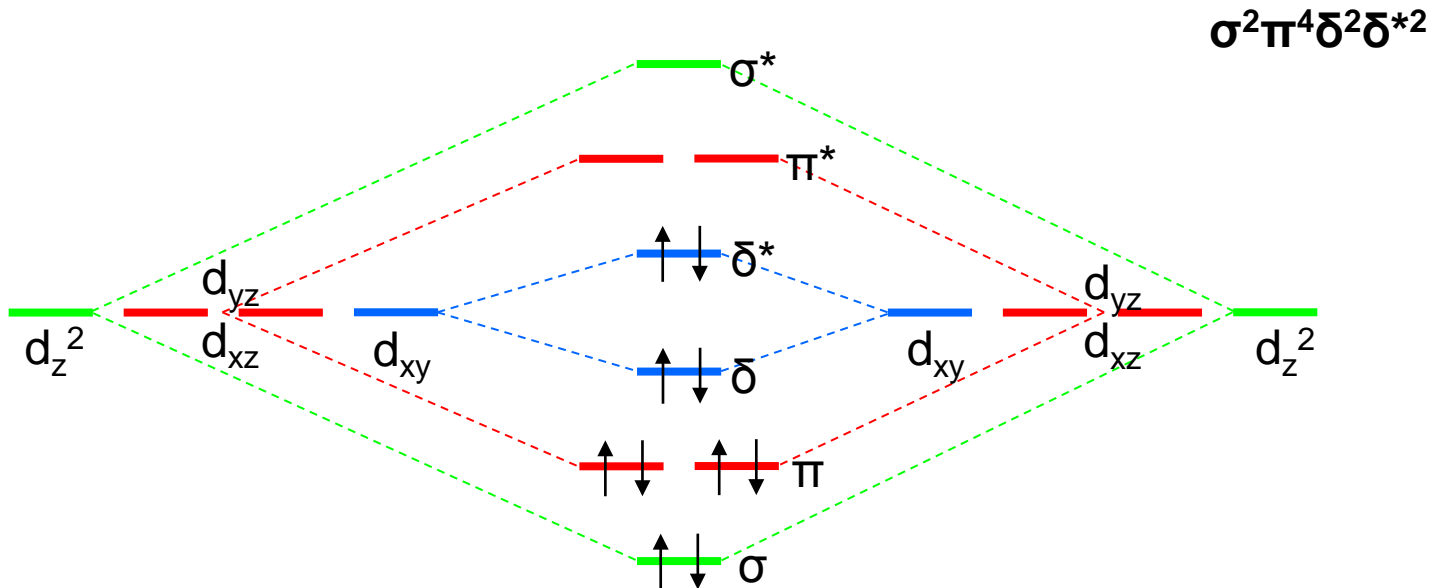
$[\text{Bu}_4\text{N}]^+$



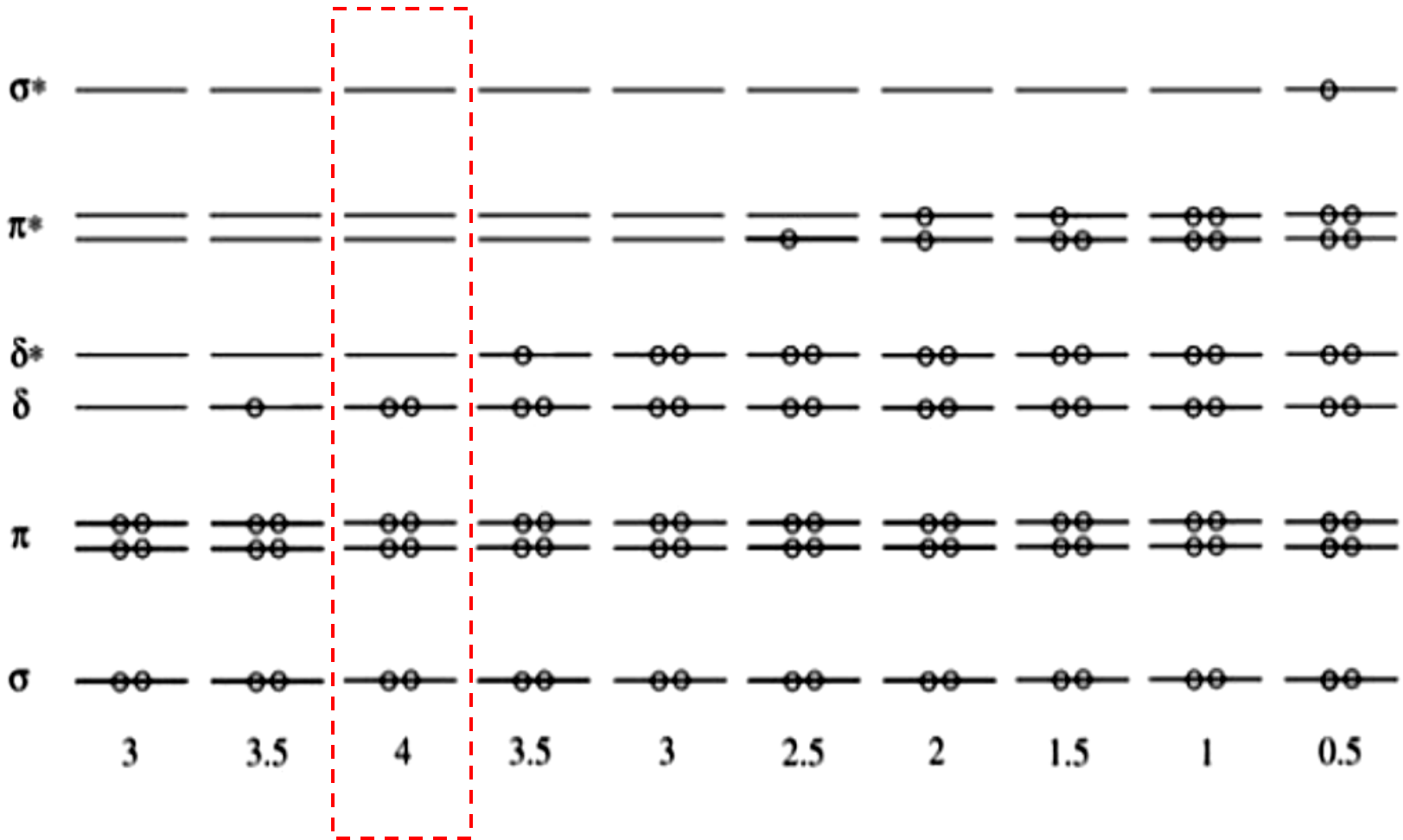
$[(\text{Ph}_3\text{P})_2\text{N}]^+$



$[\text{MePh}_3\text{N}]^+$



ΔΕΣΜΟΙ Μ-Μ



ηλεκτρονικά
ελλιπείς δεσμοί

ηλεκτρονικά πλούσιοι δεσμοί

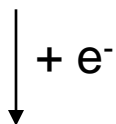
ΔΕΣΜΟΙ M-M

Electron Count	Resulting M-M Bond
d1 - d1	Single bond
d2 - d2	Double bond
d3 - d3	Triple bond
d4 - d4	Quadruple bond → optimum
d5 - d5	Triple bond
d6 - d6	Double bond (<i>M-L bonding usually dominates</i>)
d7 - d7	Single bond
d8 - d8	No bond (<i>symmetry interaction</i>)

ΔΕΣΜΟΙ M-M

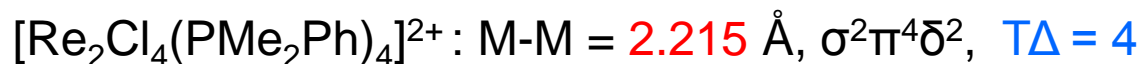
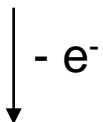
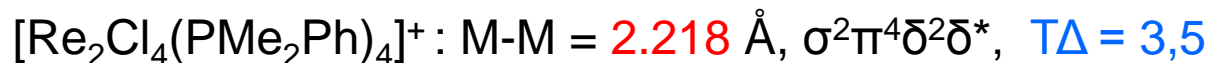
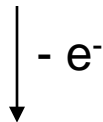
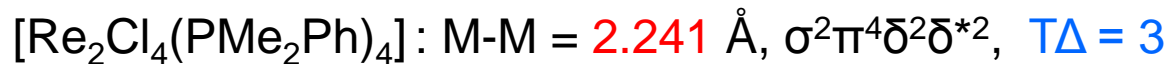
Κλασική χημεία: η απόσταση μεταξύ δύο ατόμων μικραίνει όσο μεγαλώνει η τάξη δεσμού μεταξύ τους.

Συμβαίνει το ίδιο όταν έχουμε δεσμούς M-M;



Ενώ έχουμε αύξηση της τάξης (ισχύος) του δεσμού από το $[\text{Tc}_2\text{Cl}_8]^{3-}$ στο $[\text{Tc}_2\text{Cl}_8]^{2-}$, δεν έχουμε μείωση της απόστασης, γιατί η ισχύς του δεσμού “ανταγωνίζεται” την αύξηση του αριθμού οξειδωσης (Tc_2^{5+} σε Tc_2^{6+}). Η αύξηση του αριθμού οξειδωσης έχει ως αποτέλεσμα τη συρρίκνωση - συστολή των d τροχιακών και κατ’ επέκταση τη μείωση της επικάλυψής τους.

ΔΕΣΜΟΙ M-M



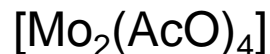
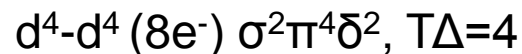
Όταν τα δ^* ηλεκτρόνια απομακρυνθούν η τυπική τάξη του δεσμού αλλάζει από 3.0, διαμέσου του 3.5, σε 4.0, αλλά οι αλλαγές στην απόσταση των Re είναι πολύ μικρές. Αυτό οφείλεται στο γεγονός ότι ταυτόχρονα ο αριθμός οξειδωσης των μεταλλικών ατόμων αυξάνεται, οπότε προξενείται συρρίκνωση των d-τροχιακών και έτσι η επικάλυψη γίνεται μικρότερη. Η εξασθένιση του δεσμού αντισταθμίζει κατά προσέγγιση την ισχυροποίηση την οποία αναμέναμε λόγω της απομακρύνσεως αντιδεσμικών ηλεκτρονίων.

Με αύξηση του φορτίου από +1 σε +2 δεν έχουμε τόσο μεγάλη συρρίκνωση των d τροχιακών, όσο μετά την πρώτη οξείδωση (από 0 σε +1), γι' αυτό τη απόσταση Re-Re παραμένει σχεδόν η ίδια. **Ανταγωνισμός τάξης δεσμού – αριθμού οξειδωσης.**

Paddlewheel structures



$$\text{Mo}^{n+}: 2x + 4(-1) = 0 \Rightarrow 2x = +4 \Rightarrow x = +2$$



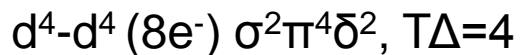
Οι υποκαταστάτες AcO^- δίνουν e^- στη διμεταλλική πλειάδα, αυτή ανακουφίζεται από το θετικό φορτίο ($4+$) με αποτέλεσμα να επεκτείνονται τα τροχιακά \Rightarrow πολύ ισχυρός δεσμός.

Ο δεσμός Mo-L είναι πολύ ευκίνητος.
Το σύμπλοκο $[\text{Mo}_2(\text{AcO})_4(\text{H}_2\text{O})_2]$ δεν έχει παρατηρηθεί.

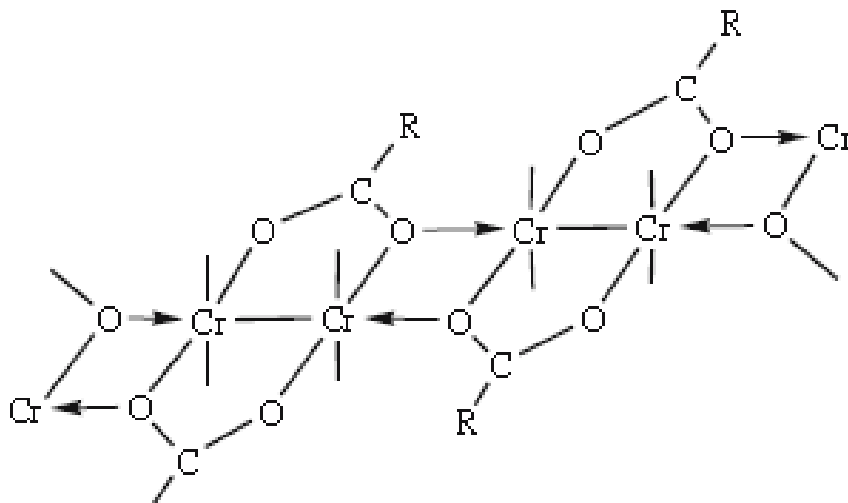
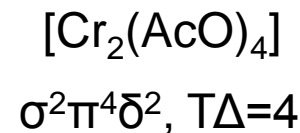
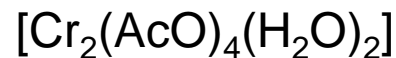
Paddlewheel structures



$$\text{Cr}^{n+}: 2x + 4(-1) = 0 \Rightarrow 2x = +4 \Rightarrow x = +2$$

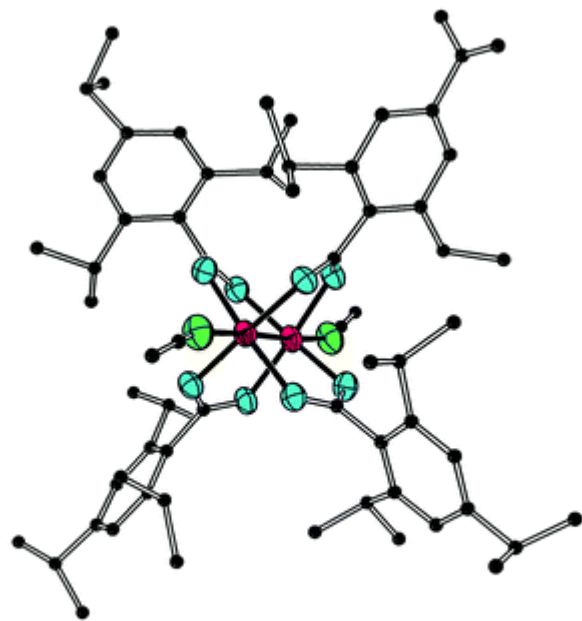


θέρμανση
→

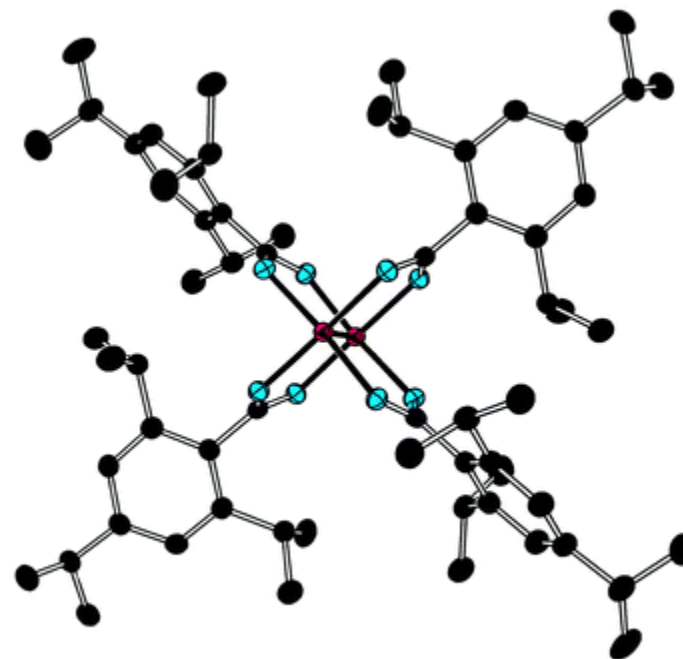
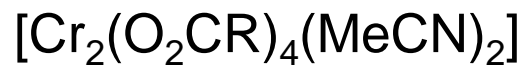


Πολυμερίζεται απουσία αξονικών υποκαταστατών

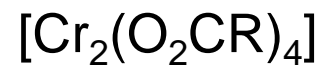
Paddlewheel structures



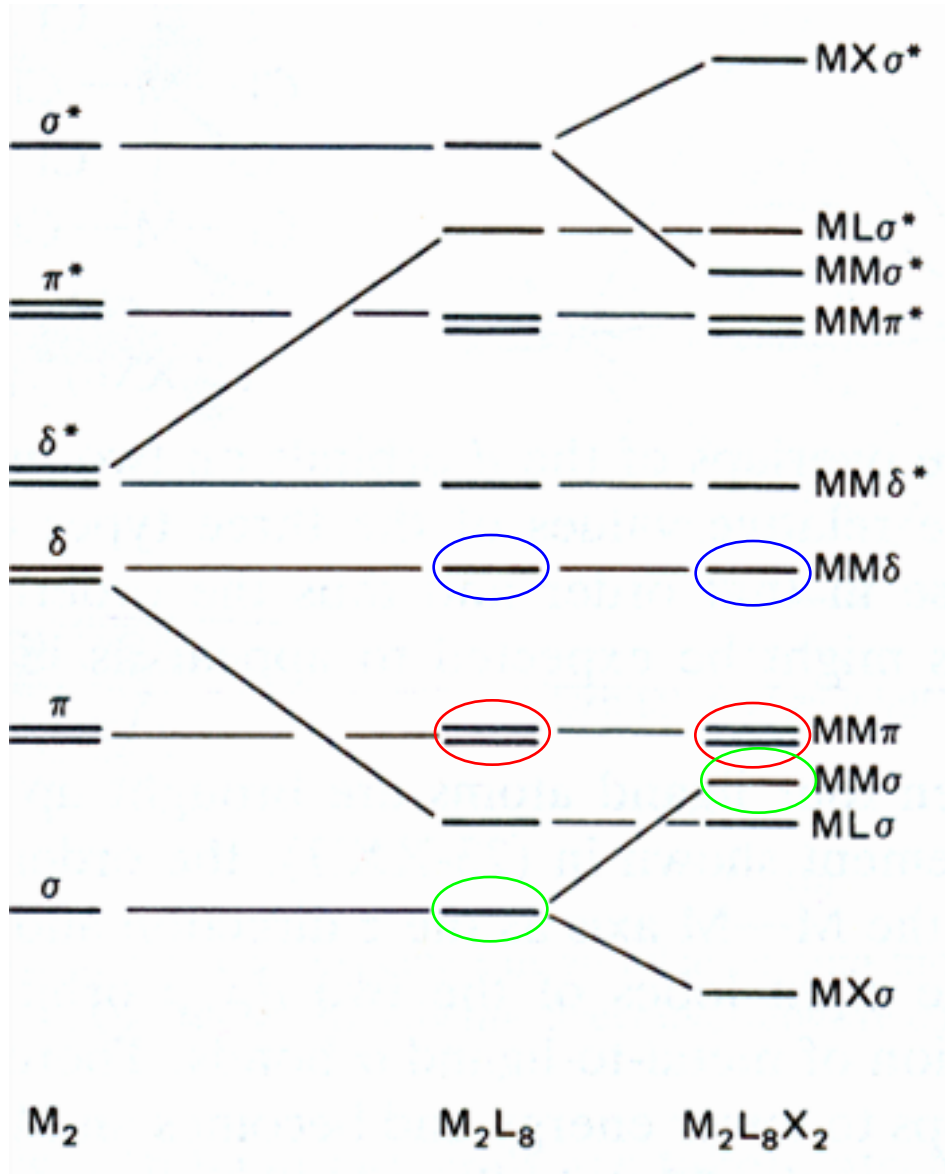
Cr-Cr = 2.3892(2) Å



Cr-Cr = 1.9662(5) Å

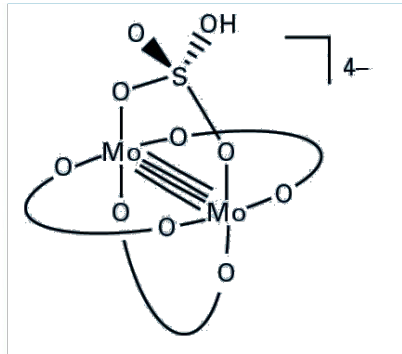
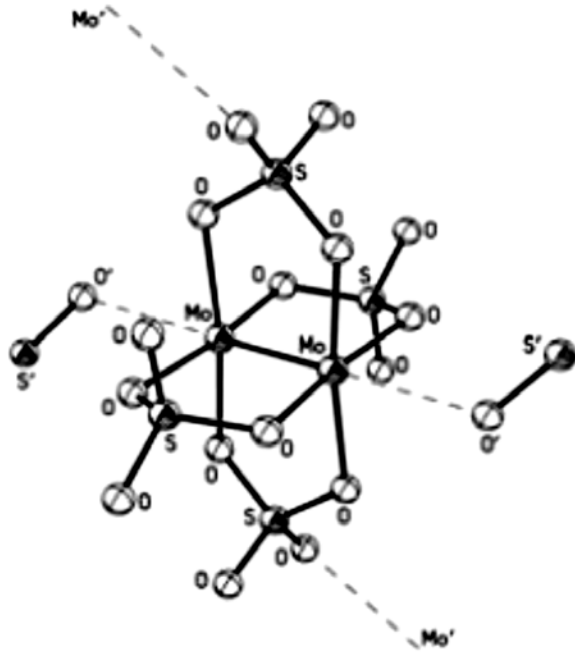


ΔΕΣΜΟΙ M-M



Ο αξονικός υποκαταστάτης **εξασθενεί το δεσμό M-M**. Δεν απαιτείται ενέργεια γιατί παράλληλα σταθεροποιείται ο σ-δεσμός M-X.

Paddlewheel structures

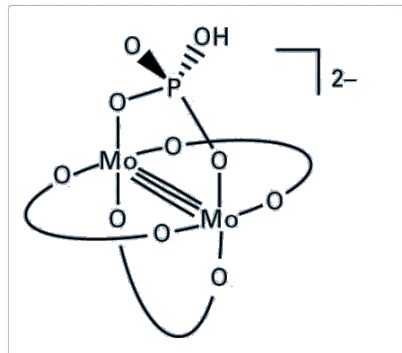


Mo(II) d⁴

$\sigma^2\pi^4\delta^2$

$T\Delta = 4$

Mo-Mo = 2.11 Å



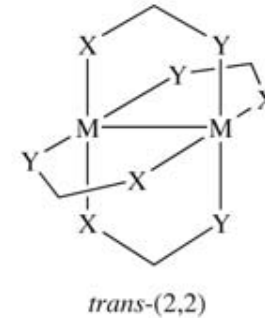
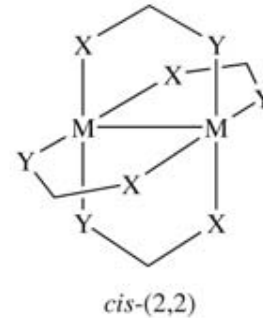
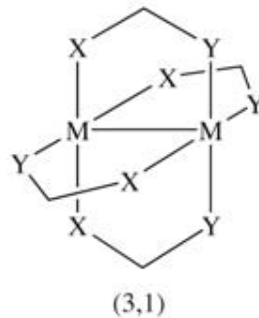
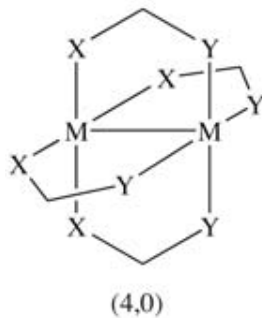
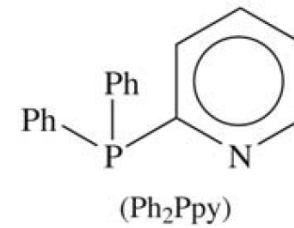
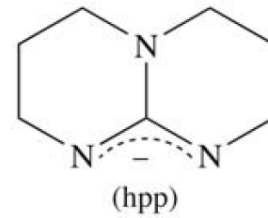
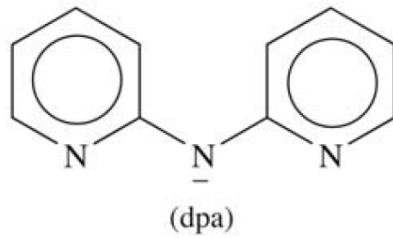
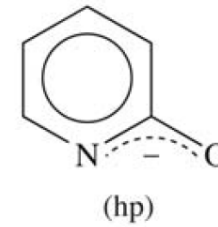
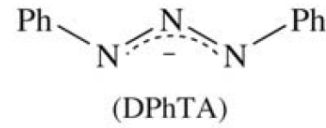
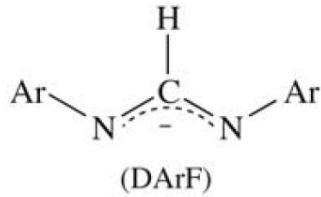
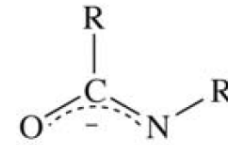
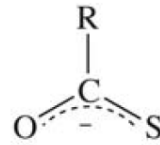
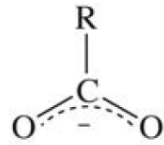
Mo(III) d³

$\sigma^2\pi^4$

$T\Delta = 3$

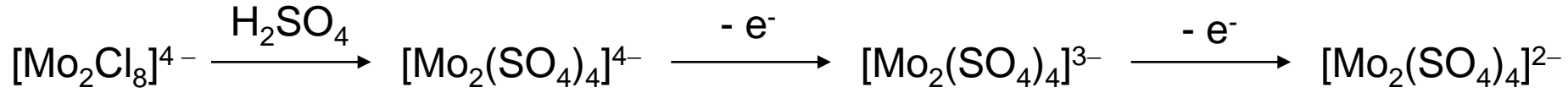
Mo-Mo = 2.22 Å

Paddlewheel structures



Τοποϊσομερή

Paddlewheel structures



Mo(II) d^4

$\sigma^2\pi^4\delta^2$

$T\Delta = 4$

Mo-Mo = 2.11 Å

διαμαγνητικό

Mo(II)/Mo(III) d^4/d^3

$\sigma^2\pi^4\delta$

$T\Delta = 3.5$

Mo-Mo = 2.16 Å

παραμαγνητικό

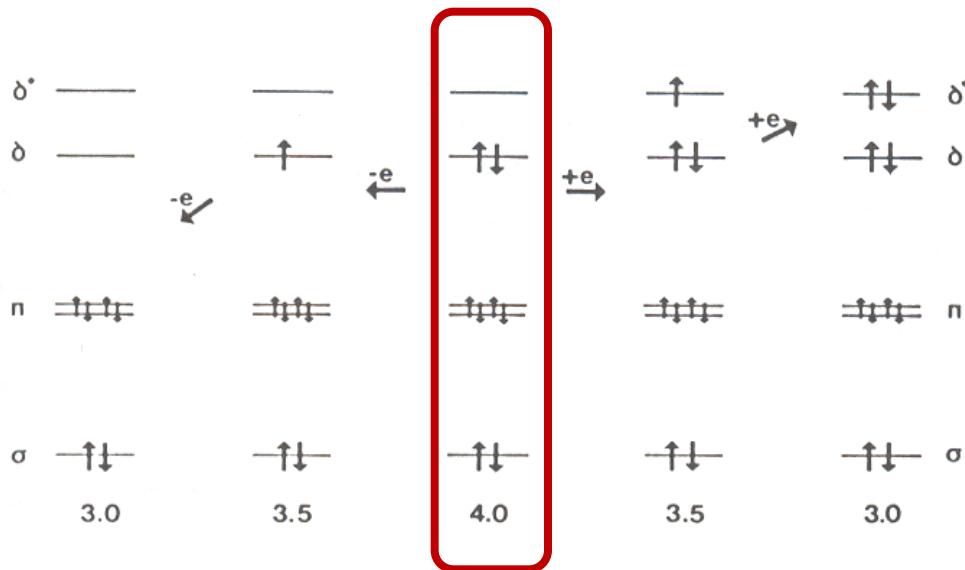
Mo(III) d^3

$\sigma^2\pi^4$

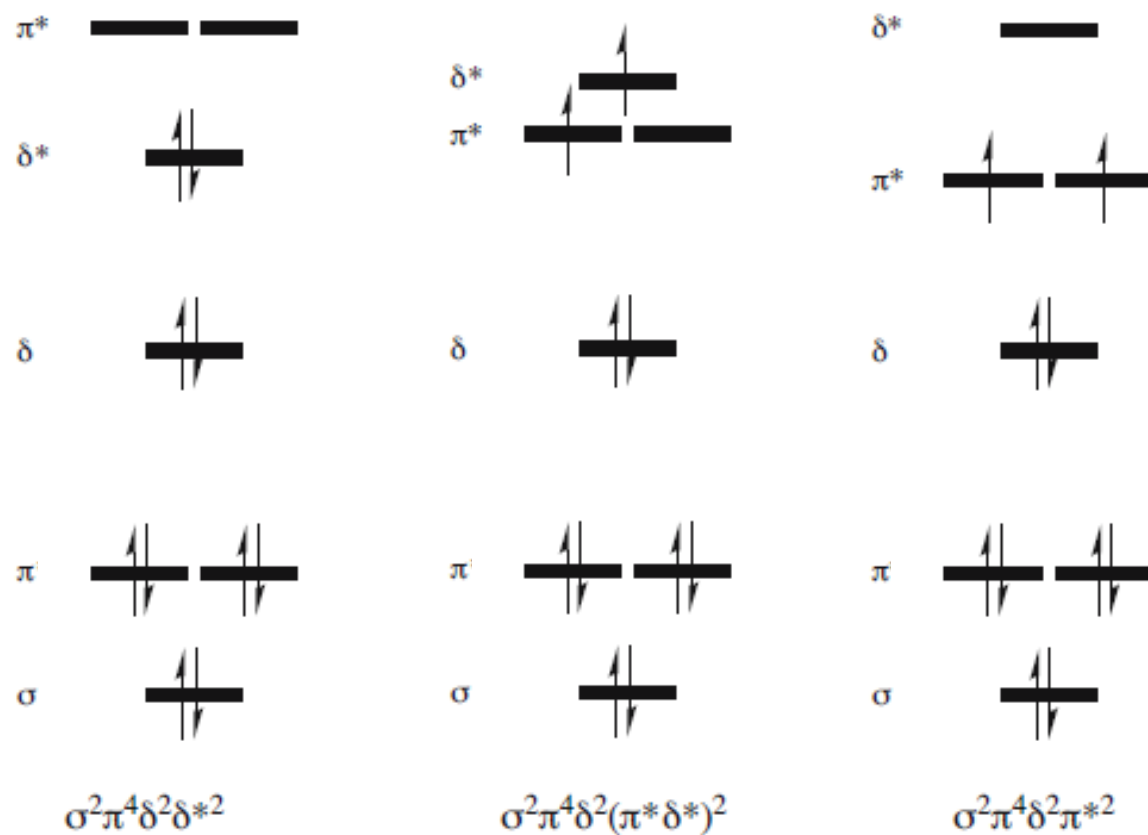
$T\Delta = 3$

Mo-Mo > 2.16 Å

διαμαγνητικό

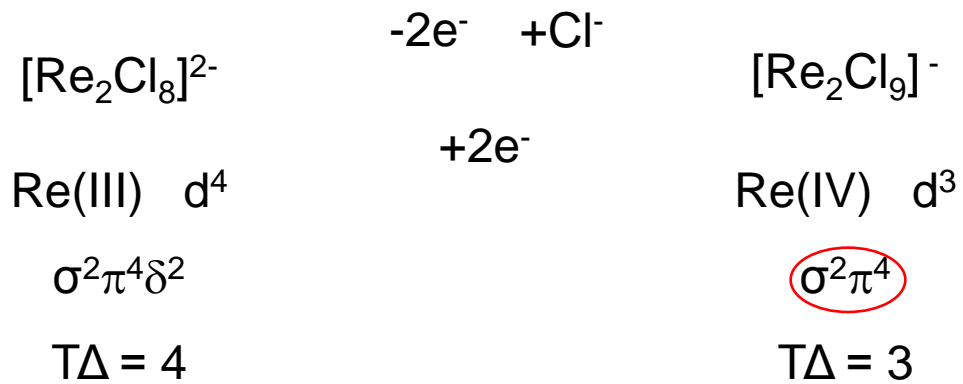


Αλλάζει η $T\Delta$, όχι όμως η δομή.



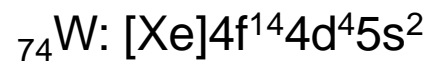
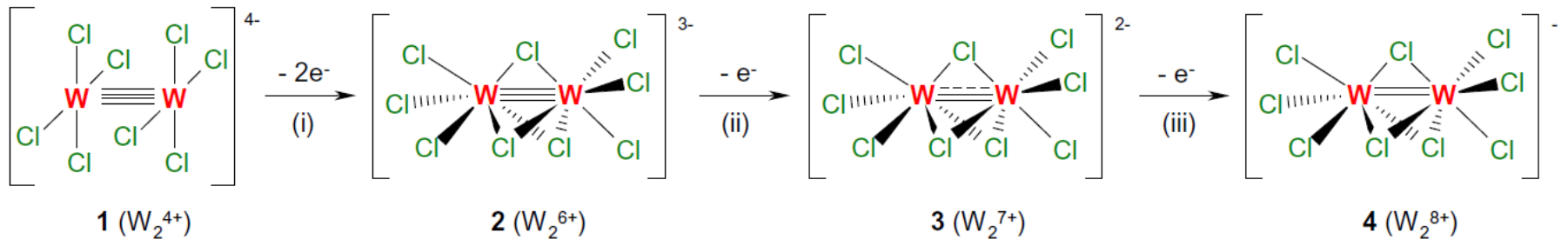
Scheme 10.4. Possible ground state configurations for Os_2^{6+} paddlewheel species.

Face-Sharing Bioctahedra (FSBO)

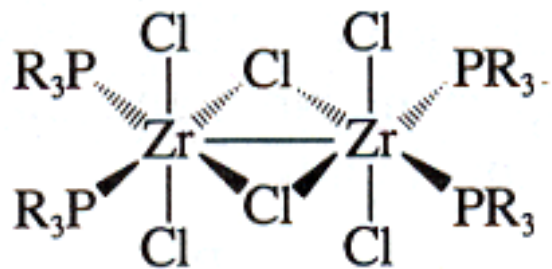


Αλλάζει η $T\Delta$, αλλάζει όμως και η δομή.

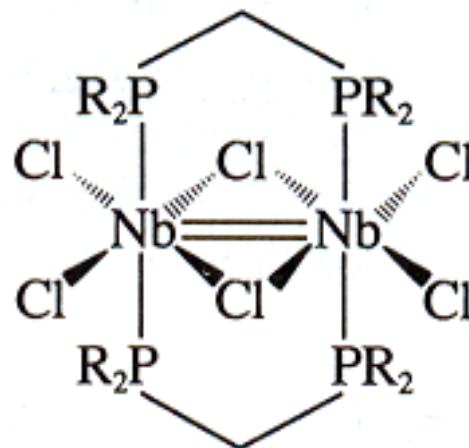
FSBO



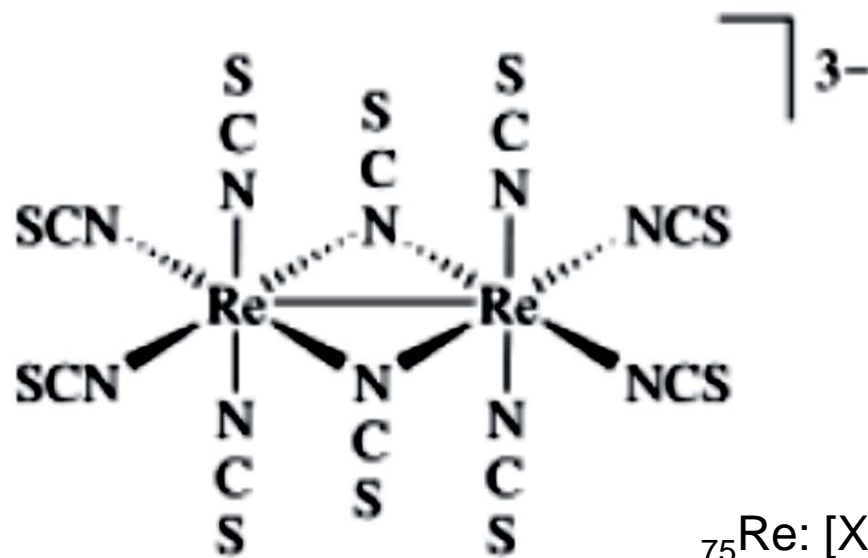
Edge-Sharing Bioctahedra (ESBO)



⁴⁰Zr: [Kr]4d²5s²

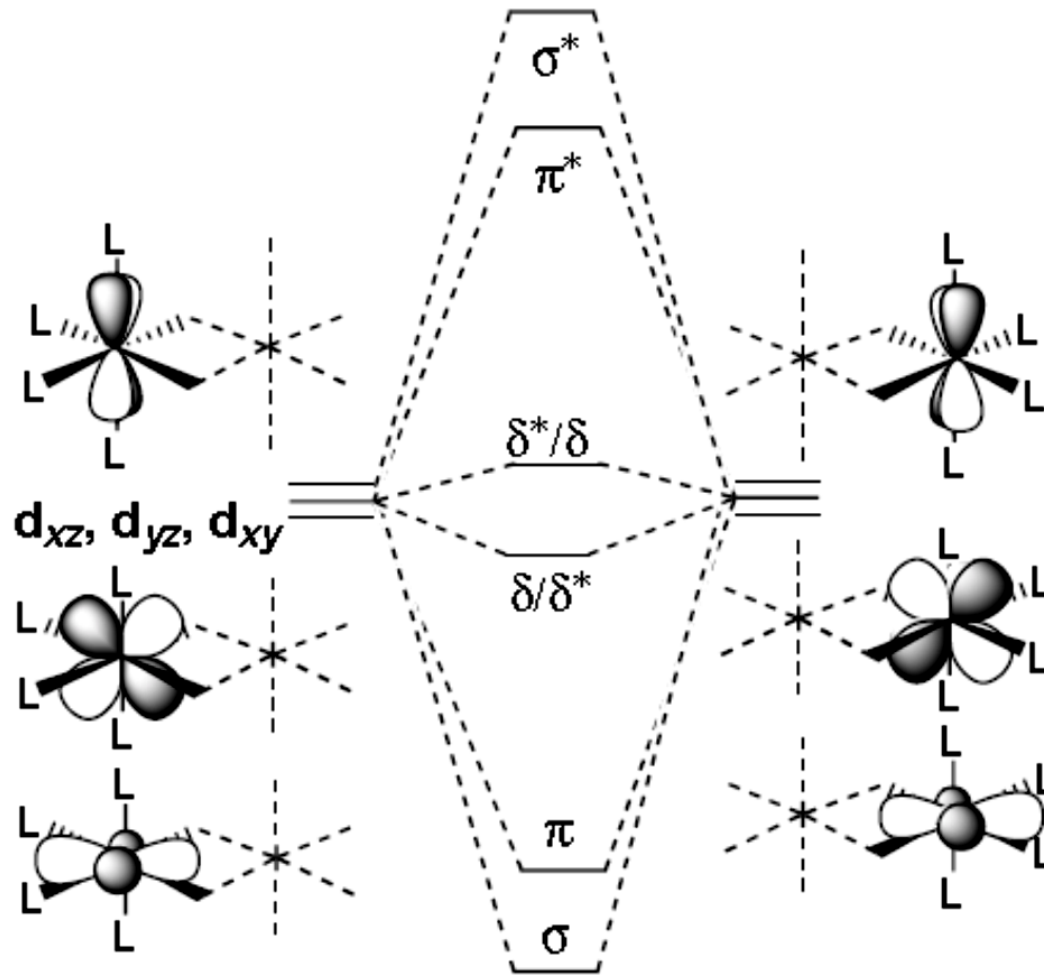


⁴¹Nb: [Kr]4d⁴5s¹



⁷⁵Re: [Xe]4f¹⁴5d⁵6s²

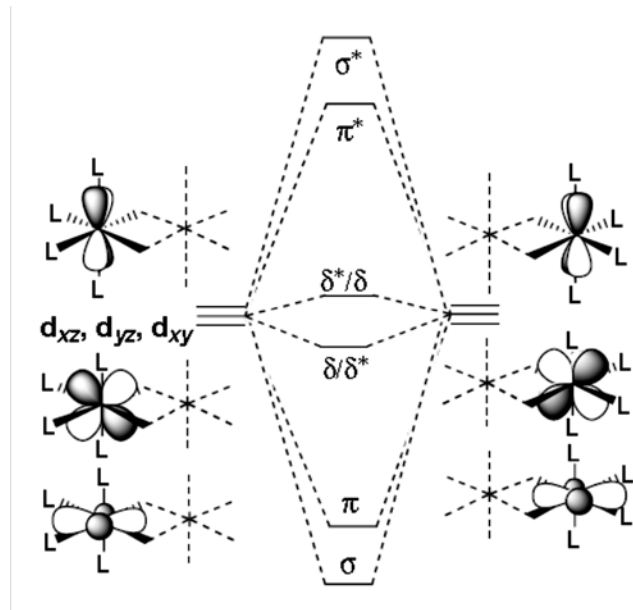
Edge-Sharing Bioctahedra (ESBO)



Το d_{z^2} δεν συμμετέχει...

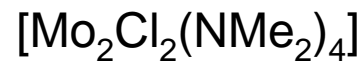
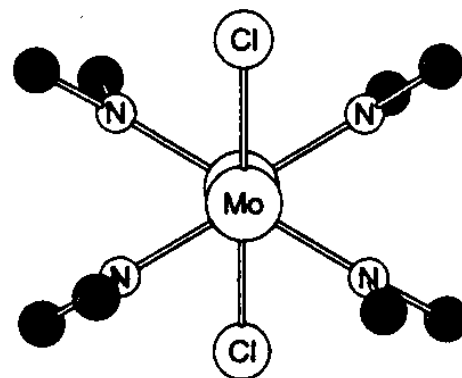
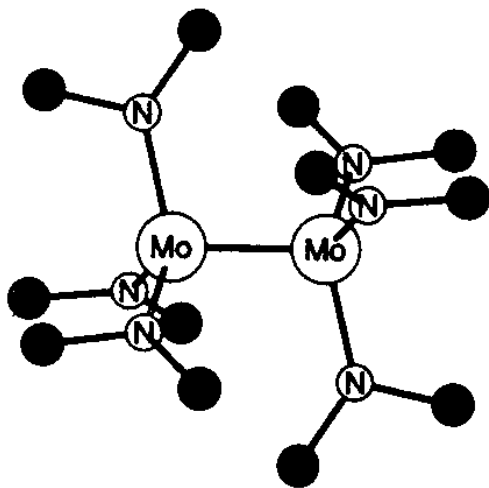
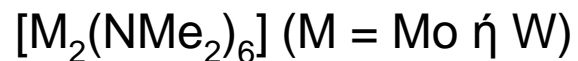
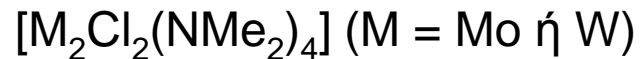
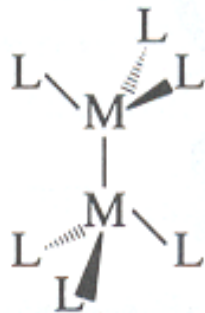
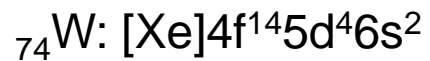
Edge-Sharing Bioctahedra (ESBO)

Σε περίπτωση όπου δυο d^4 μεταλλικά άτομα αλληλεπιδρούν έχουμε ένα καθαρά διπλό δεσμό γιατί και τα δυο, τα δ και δ^* τροχιακά, θα είναι συμπληρωμένα. Το προηγούμενο διάγραμμα των ενεργειακών επιπέδων δείχνει ότι τα δ -τροχιακά είναι πιο σταθερά από τα δ^* , αλλά λαμβάνοντας υπόψιν μας τις διαφορετικές αλληλεπιδράσεις των δυο αυτών τροχιακών με τα τροχιακά των υποκαταστατών η σειρά μπορεί (και στις περισσότερες περιπτώσεις αυτό γίνεται) να αναστραφεί. Έτσι, σε ένα d^3 - d^3 σύστημα η τάξη του δεσμού είναι μάλλον 1 και όχι 3. Τα τροχιακά δ και δ^* βρίσκονται πολύ κοντά ενεργειακά και σε ορισμένες περιπτώσεις αυτά είναι τόσο κοντά που μια απλή (singlet) κατάσταση (δ^2 ή δ^{*2}) και μια τριπλή (triplet) κατάσταση ($\delta\delta^*$) διαφέρουν μονάχα λίγες εκατοντάδες cm^{-1} , με αποτέλεσμα να παρατηρείται μια ισορροπία spin-state (spin-καταστάσεως).



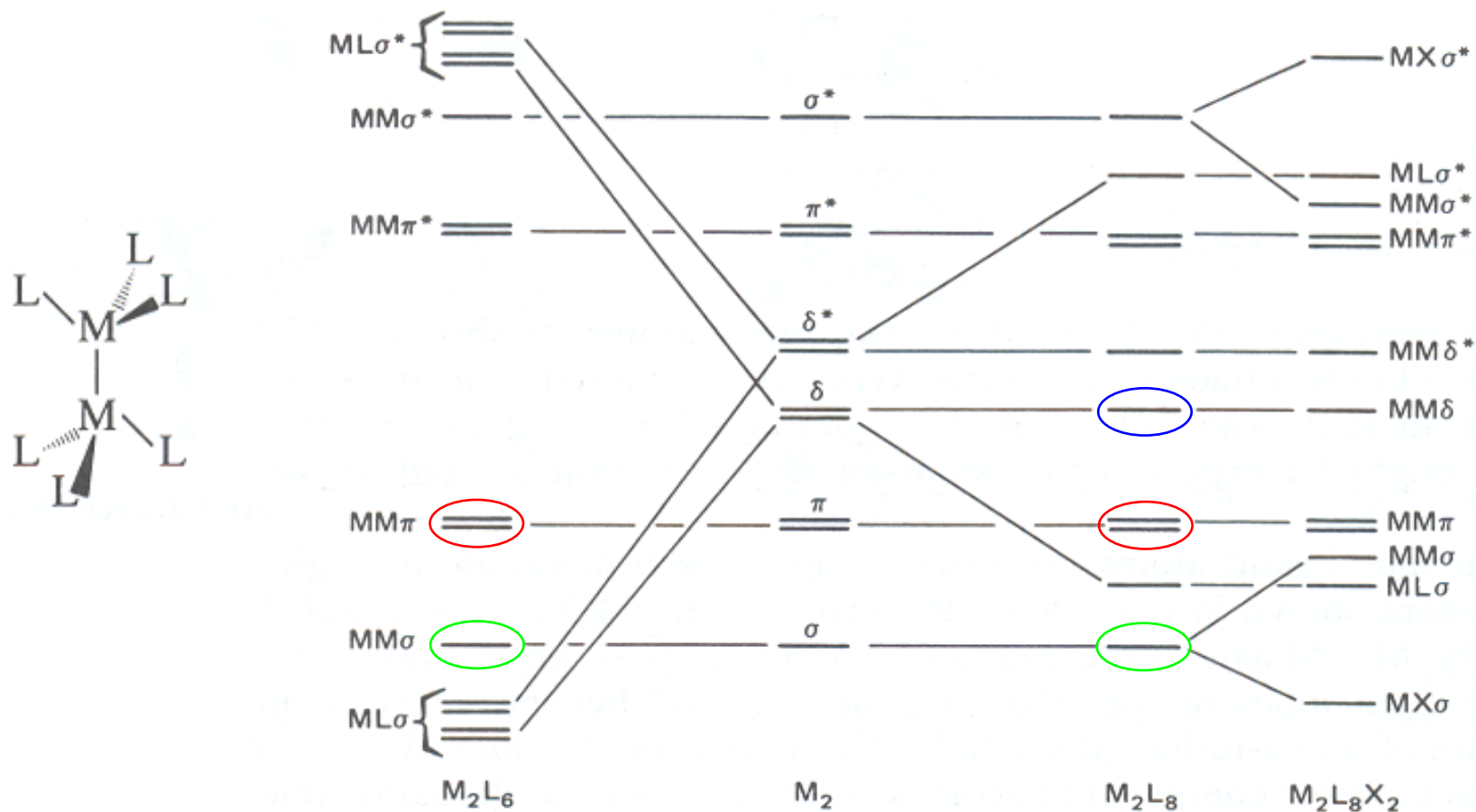
ΣΥΜΠΛΟΚΑ ΤΥΠΟΥ ΑΙΘΑΝΙΟΥ

Trigonal Antiprismatic Structures



ΣΥΜΠΛΟΚΑ ΤΥΠΟΥ ΑΙΘΑΝΙΟΥ

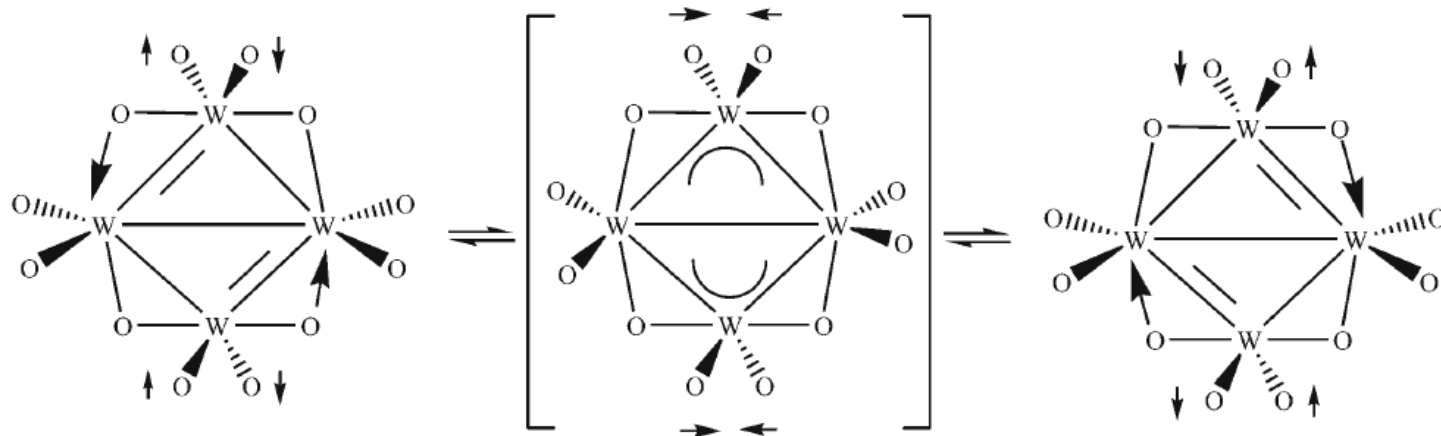
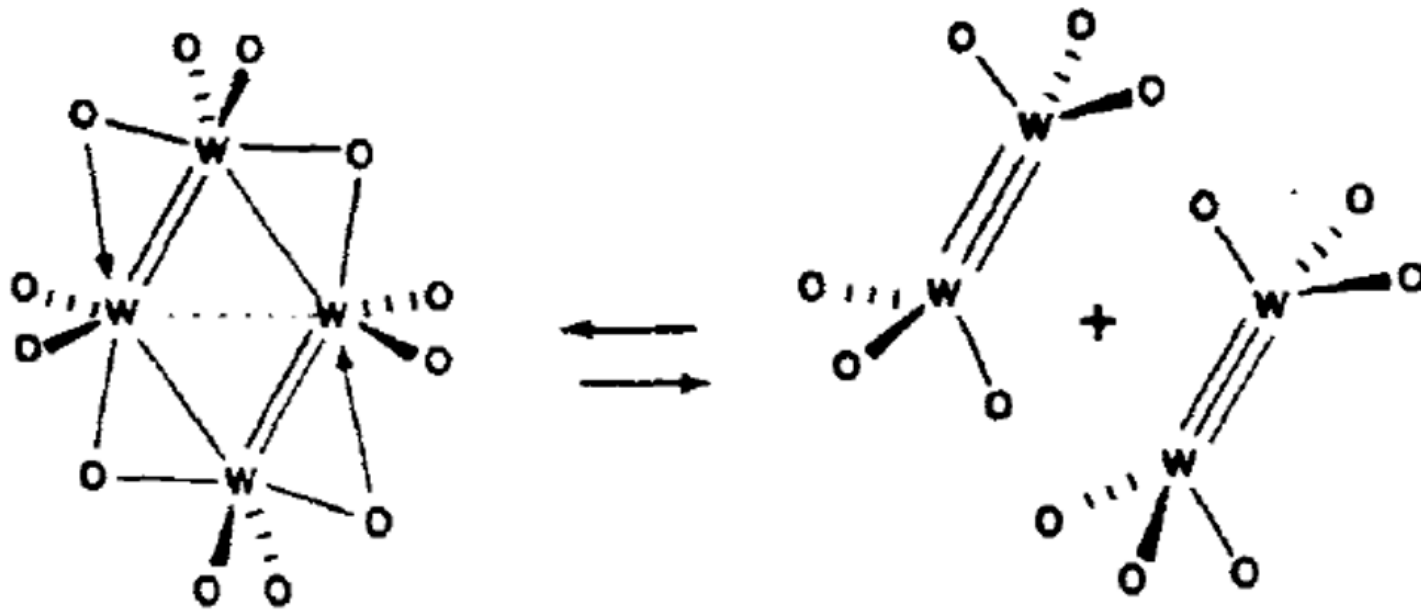
Trigonal Antiprismatic Structures



Το πλησίασμα έξι υποκαταστατών κατά τον τρόπο που φαίνεται προξενεί μετατόπιση των ενεργειών των δ και δ^* τροχιακών και αφήνει τρία M-M δεσμικού τύπου τροχιακά, σ και π (διπλά εκφυλισμένο). Έτσι ευνοείται ο σχηματισμός τριπλών δεσμών με απεικόνιση $\sigma^2\pi^4$. Ενώσεις που ανήκουν σε αυτή την τάξη σχηματίζονται κυρίως από το μολυβδαίνιο (III) και από το βολφράμιο.

ΣΥΜΠΛΟΚΑ ΤΥΠΟΥ ΑΙΘΑΝΙΟΥ

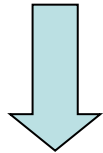
Trigonal Antiprismatic Structures



ΣΥΜΠΛΟΚΑ ΜΙΚΤΟΥ ΣΘΕΝΟΥΣ



$$\text{Ru}^{n+}: 2x + 4(-1) + (-1) = 0 \Rightarrow 2x = +5 \Rightarrow x = +2.5$$

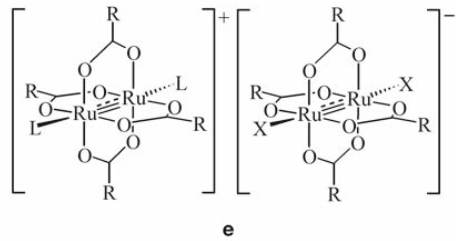
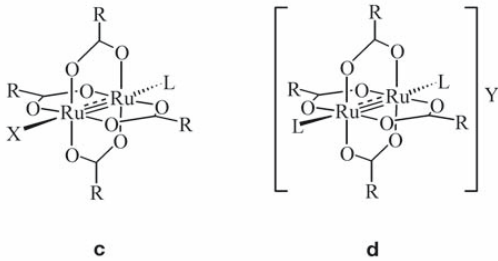
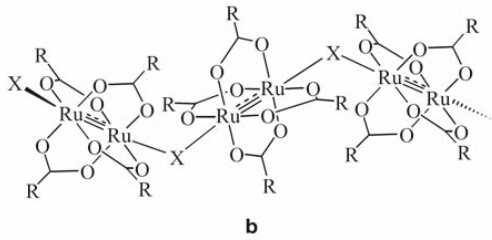
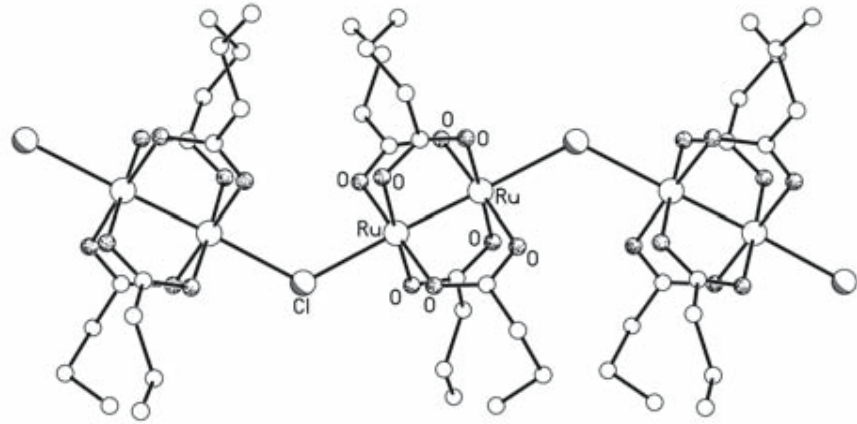
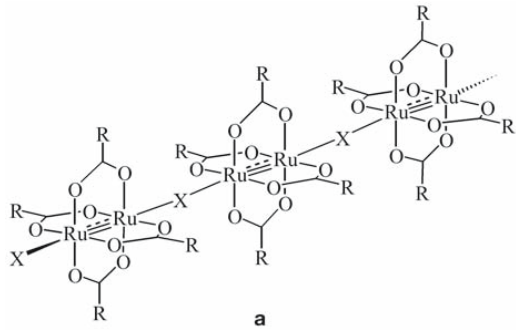


1 ασύζευκτο e^-

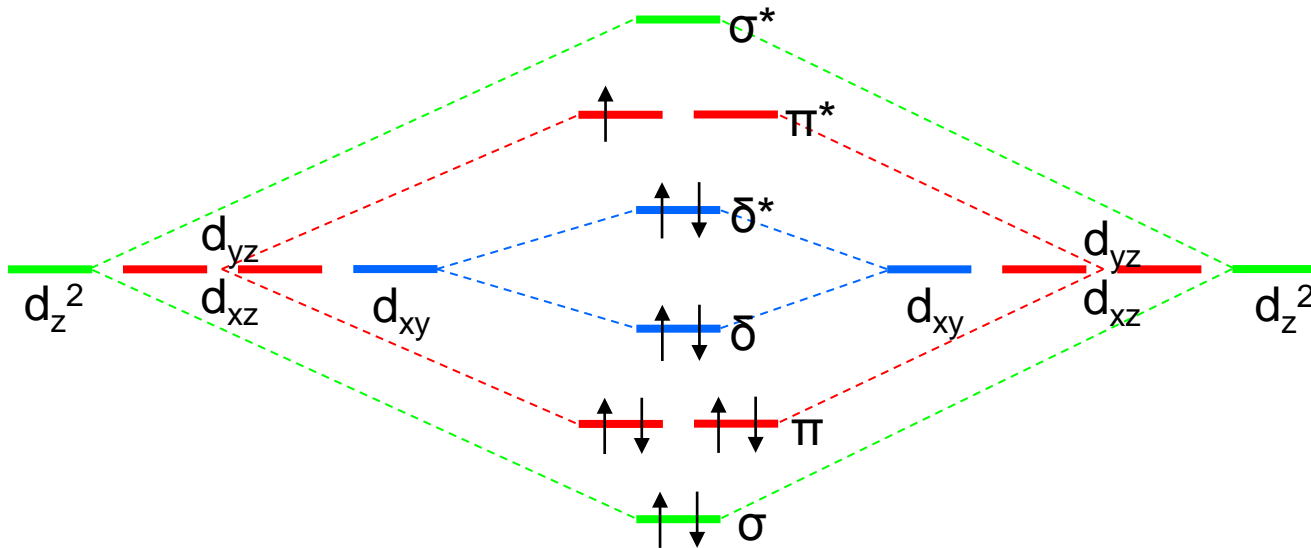
?

Μετρήσεις μαγνητικής επιδεκτικότητας
3 ασύζευκτα e^-

ΣΥΜΠΛΟΚΑ ΜΙΚΤΟΥ ΣΘΕΝΟΥΣ



ΣΥΜΠΛΟΚΑ ΜΙΚΤΟΥ ΣΘΕΝΟΥΣ



1 ασύζευκτο e^-

$$d^5-d^6 (11e^-) \sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^*, T\Delta=2,5$$



3 ασύζευκτα e^-

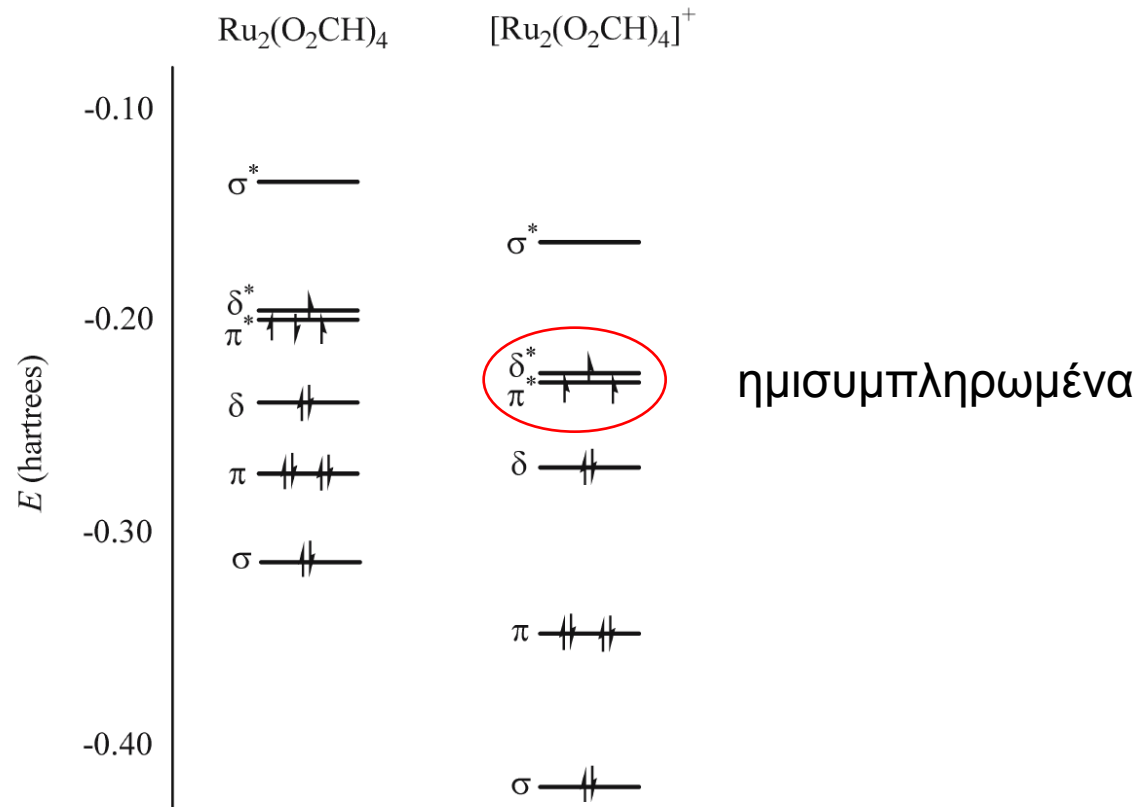
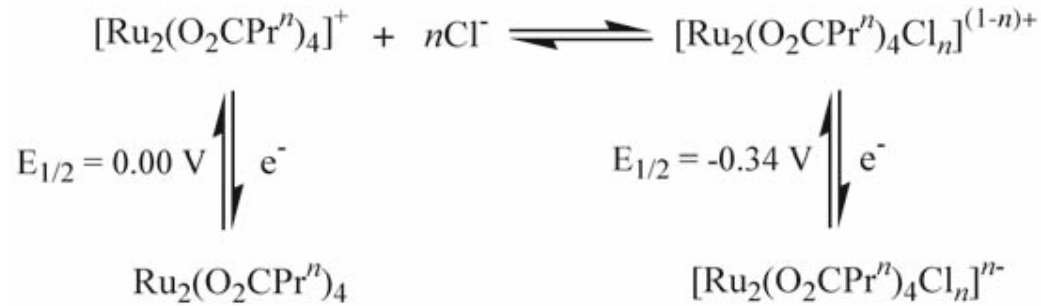
$$d^5-d^6 (11e^-) \sigma^2 \pi^4 \delta^2 \pi^{*2} \delta^*, T\Delta=2,5$$



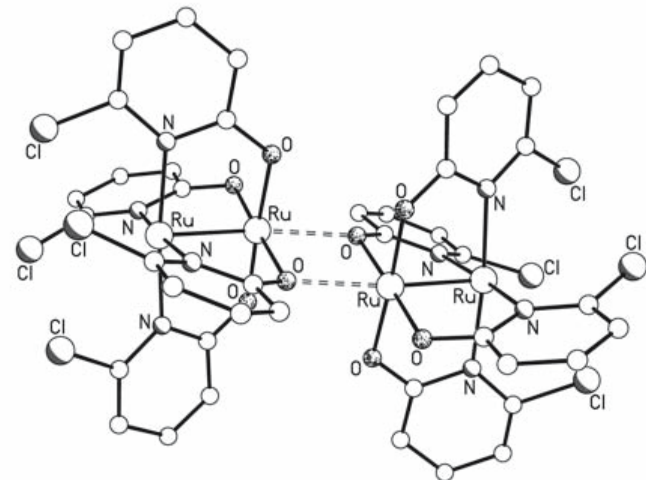
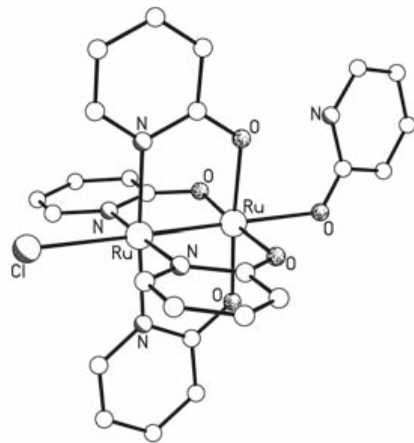
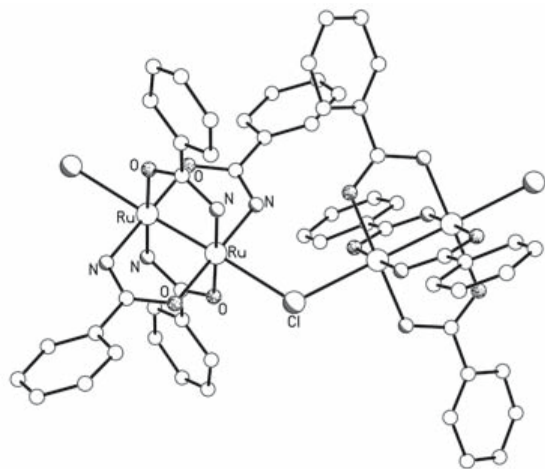
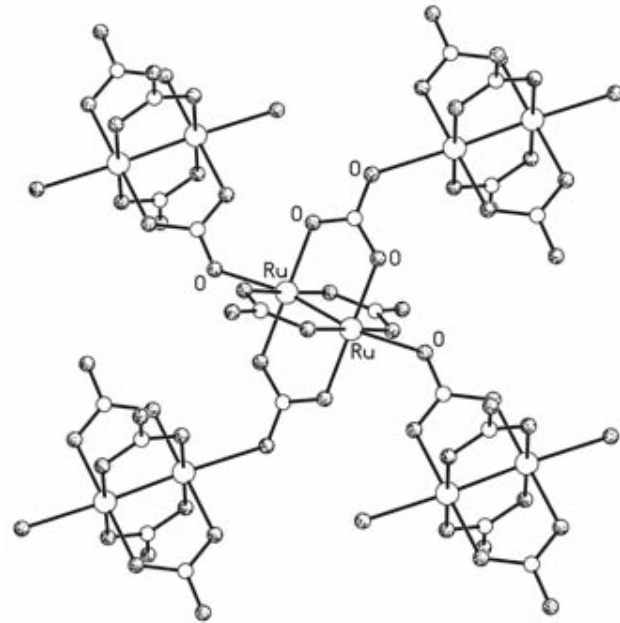
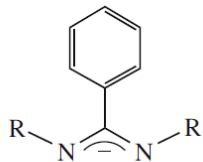
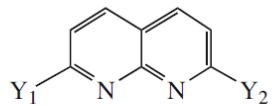
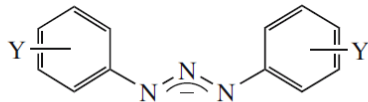
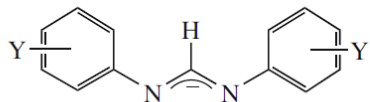
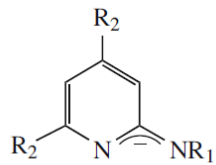
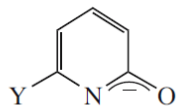
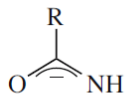
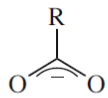
3 ασύζευκτα e^-

$$d^5-d^6 (11e^-) \sigma^2 \pi^4 \delta^2 (\pi^* \delta^*)^3 T\Delta=2,5$$

ΣΥΜΠΛΟΚΑ ΜΙΚΤΟΥ ΣΘΕΝΟΥΣ



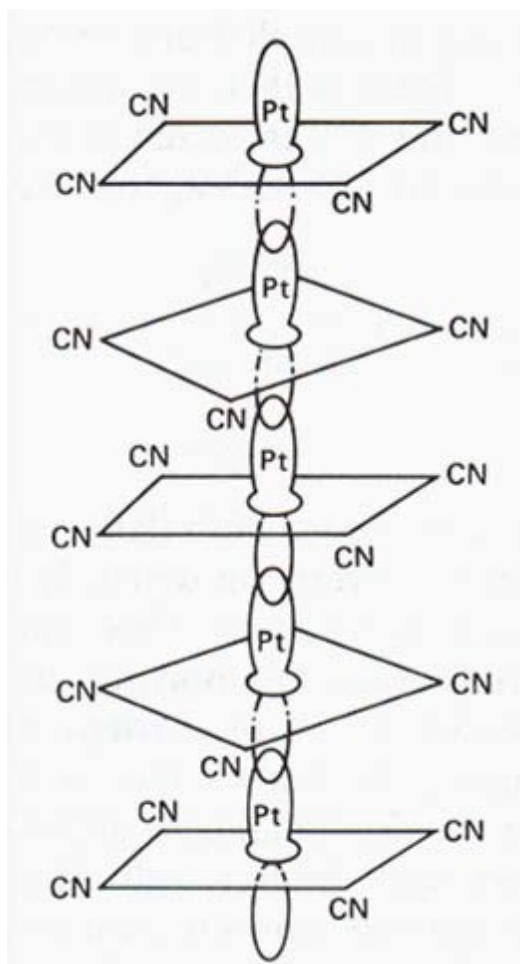
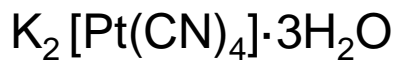
ΣΥΜΠΛΟΚΑ ΜΙΚΤΟΥ ΣΘΕΝΟΥΣ



ΜΟΝΟΔΙΑΣΤΑΤΑ ΣΤΕΡΕΑ

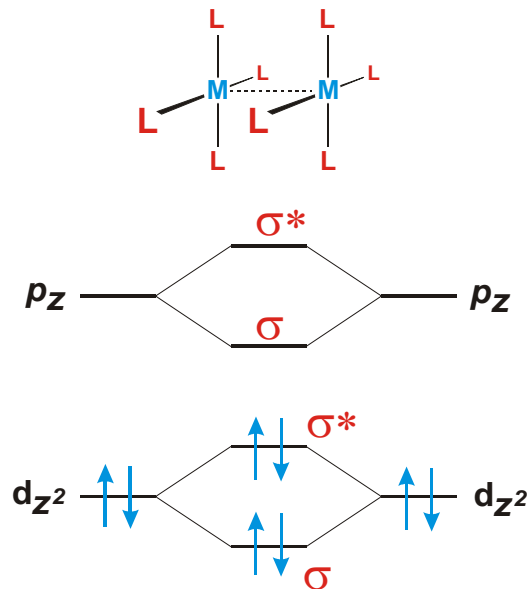
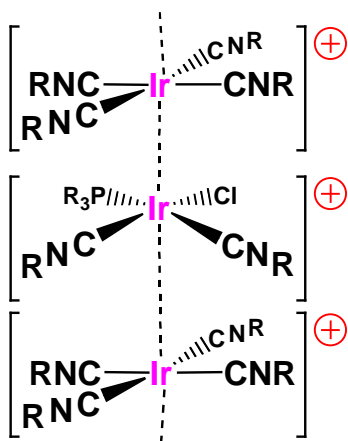
Some Tetracyanoplatinate Compounds with Stacked Anions

Complex	Pt valence	Pt—Pt (Å)	Color	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)
Pt metal	0	2.775	Metallic	$\sim 9.4 \times 10^4$
$\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$	+2.0	3.48	White	5×10^{-7}
$\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3}] \cdot 3\text{H}_2\text{O}$	+2.3	2.88	Bronze	4–830
$\text{K}_2[\text{Pt}(\text{CN})_4\text{Cl}_{0.3}] \cdot 3\text{H}_2\text{O}$	+2.3	2.87	Bronze	~ 200
$\text{K}_{1.75}[\text{Pt}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$	+2.25	2.96	Bronze	$\sim 70\text{--}100$
$\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.39}$	+2.39	2.83	Gold	Unknown



ΜΟΝΟΔΙΑΣΤΑΤΑ ΣΤΕΡΕΑ

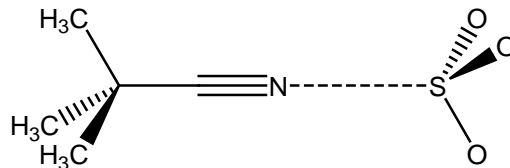
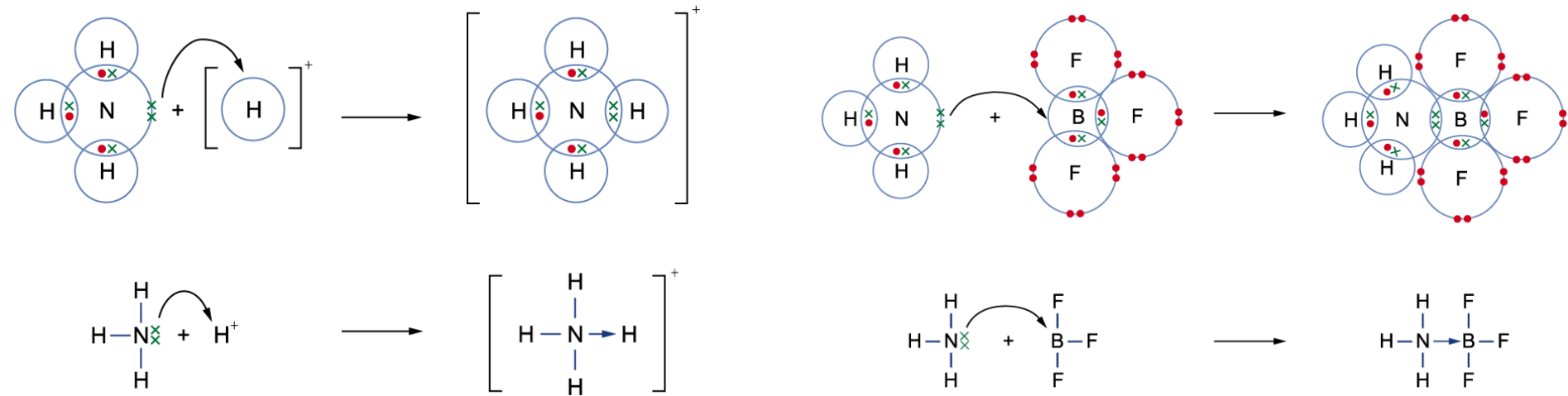
1974 Gray



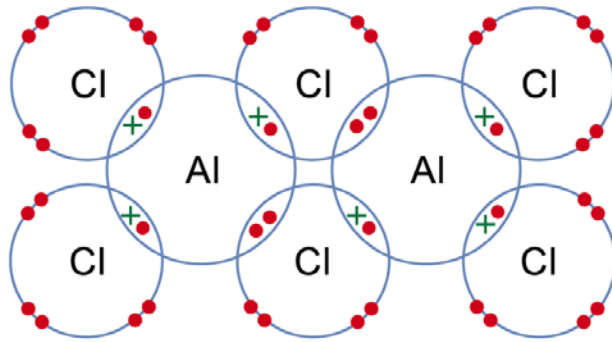
Weak M-M interactions were caused by a molecular orbital symmetry interaction between the filled σ -M-M bonding and σ^* -anti-bonding orbitals with the empty p_z σ and σ^* orbitals. The empty orbitals are pushed up in energy and the filled orbitals down in energy by this symmetry interaction. This generates a weak M-M bond – strong enough, however, to allow these complexes to form M-M bonds even in solution.

ΔΟΤΙΚΟΙ ΔΕΣΜΟΙ

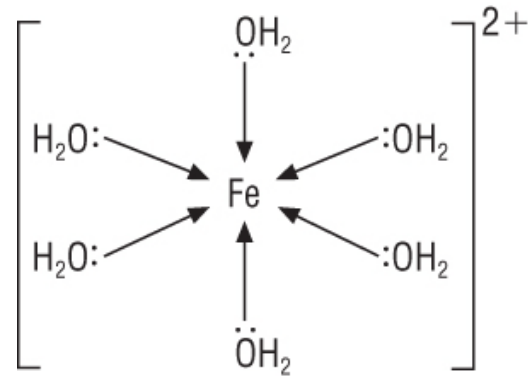
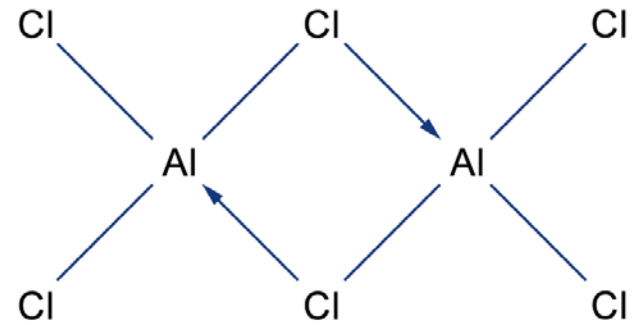
The dative covalent bond (also known as the coordinate bond) is a type of covalent bond in which the shared pair of electrons is supplied by only one of the bonded atoms.



ΔΟΤΙΚΟΙ ΔΕΣΜΟΙ

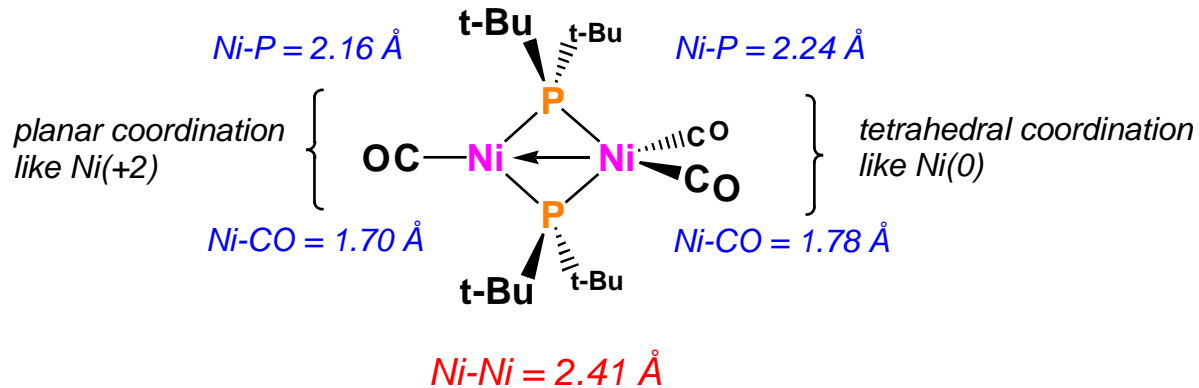


or



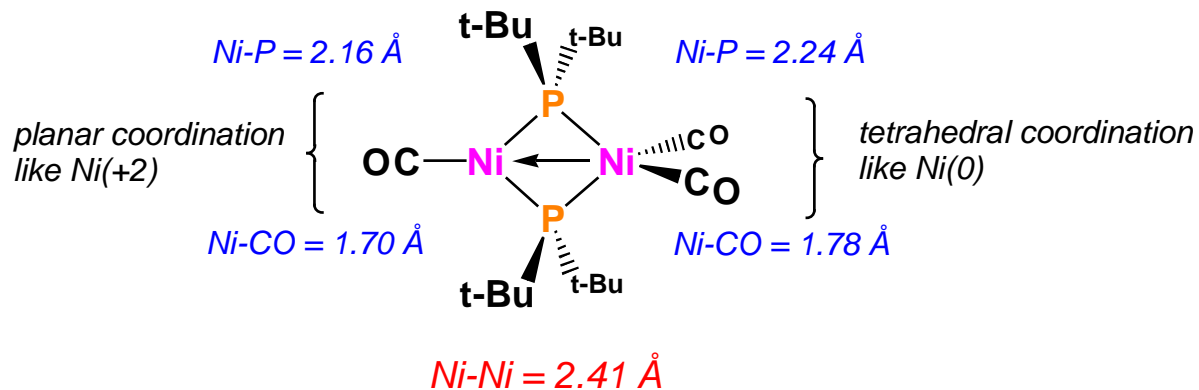
?

ΔΟΤΙΚΟΙ ΔΕΣΜΟΙ



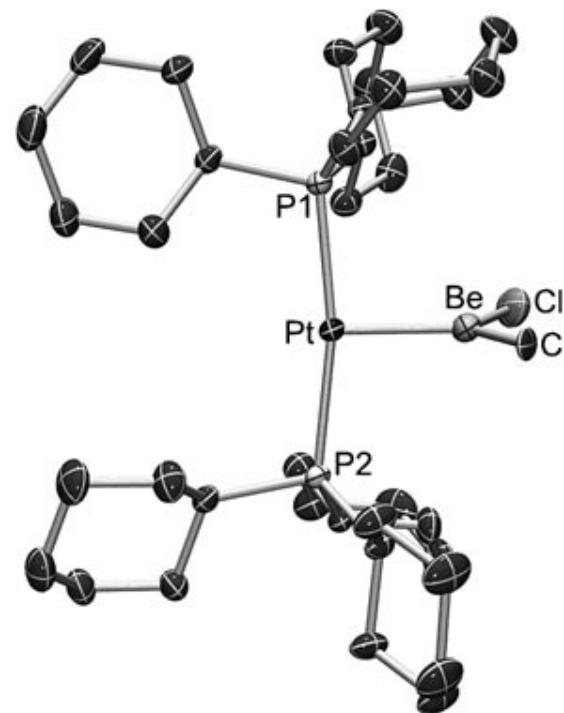
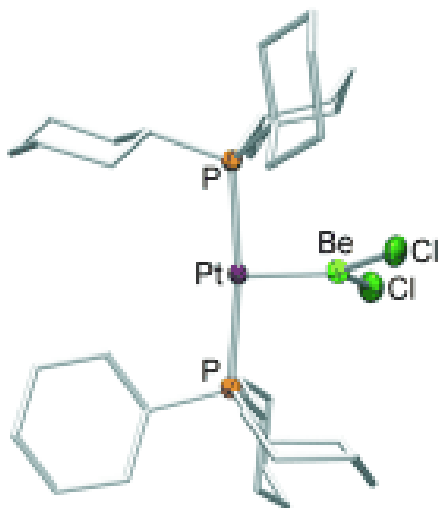
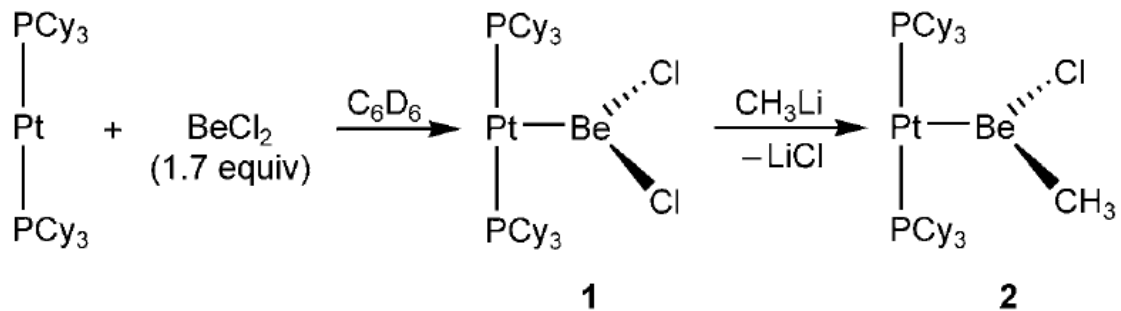
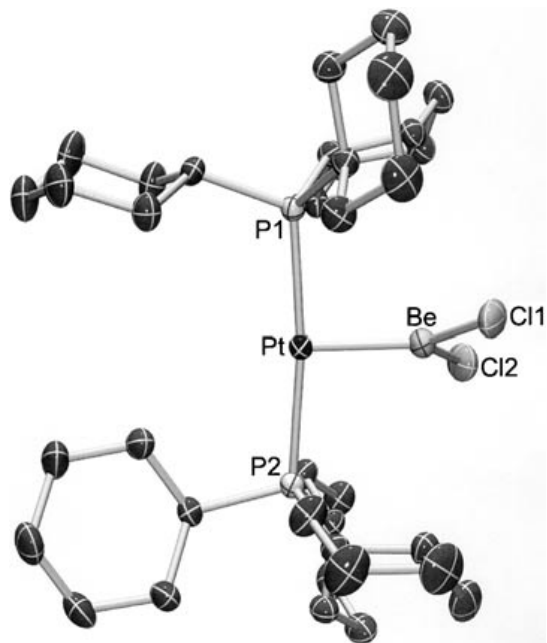
Όταν ένα μεταλλικό ιόν το οποίο έχει τουλάχιστον 2 d ηλεκτρόνια και είναι παράλληλα ηλεκτρονικά πλούσιο (κορεσμένο με 16 ή 18e⁻) βρεθεί κοντά σε ένα μεταλλικό ιόν το οποίο είναι ηλεκτρονικά φτωχό (ακόρεστο), το ηλεκτρονικά πλούσιο μεταλλικό ιόν μπορεί να δώσει ένα ελεύθερο ζεύγος d ηλεκτρονίων στο ακόρεστο μεταλλικό ιόν για να δημιουργηθεί ένας δοτικός M→M δεσμός.

ΔΟΤΙΚΟΙ ΔΕΣΜΟΙ



Covalent M-M Bonding				Dative			
Left Ni		Right Ni		Left Ni		Right Ni	
Ni(+1)	d ⁹	Ni(+1)	d ⁹	Ni(+2)	d ⁸	Ni(0)	d ¹⁰
[μ-PR ₂] ⁻	2e ⁻	[μ-PR ₂] ⁻	2e ⁻	2[μ-PR ₂] ⁻	4e ⁻	2μ-PR ₂	4e ⁻
μ-PR ₂	2e ⁻	μ-PR ₂	2e ⁻	CO	2e ⁻	2CO	4e ⁻
CO	2e ⁻	2CO	4e ⁻	Ni←Ni(0)	2e ⁻		
M-M	1e ⁻	M-M	1e ⁻				
Total	16e⁻	Total	18e⁻	Total	16e⁻	Total	18e⁻

ΔΟΤΙΚΟΙ ΔΕΣΜΟΙ

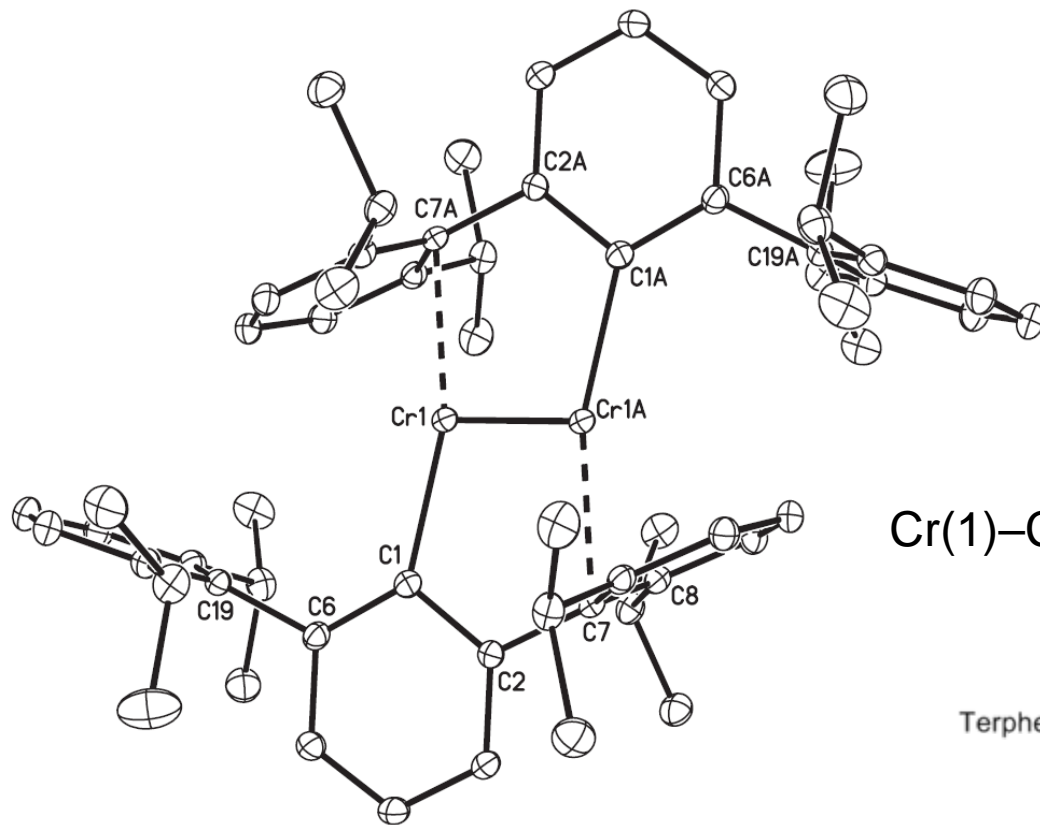


ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ

$d^5 - d^5$

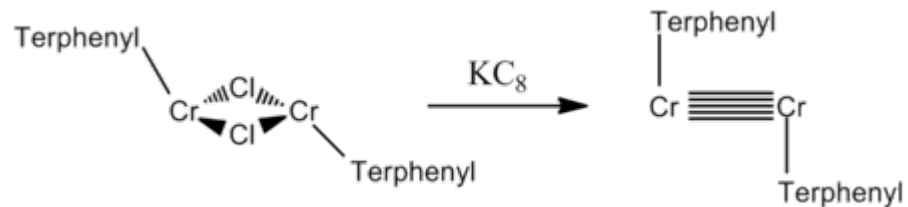
φορτίο

αριθμός ένταξης

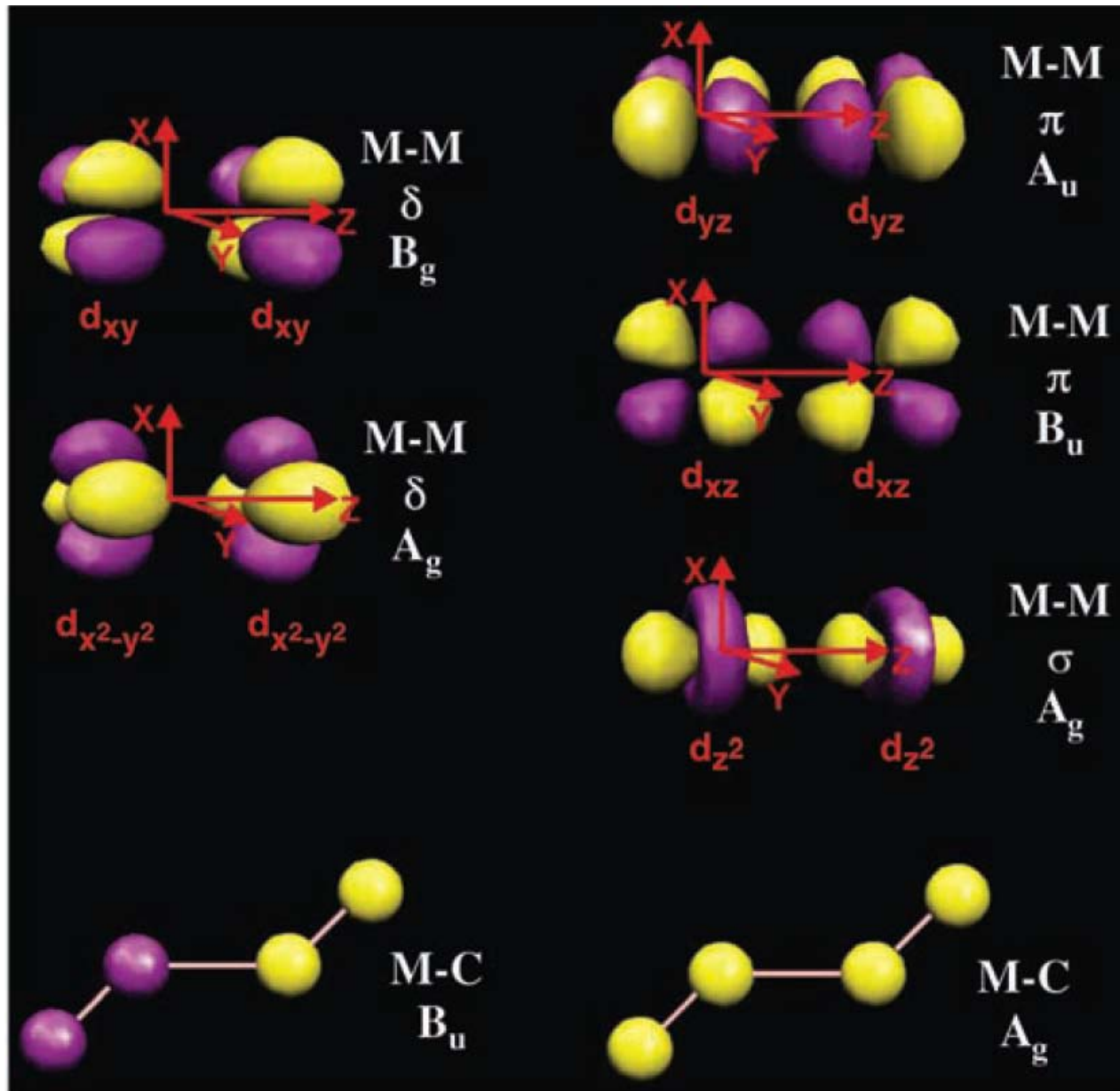


Cr(1)–Cr(1A), 1.8351(4) Å

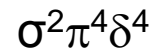
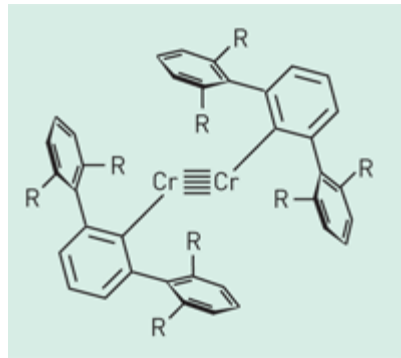
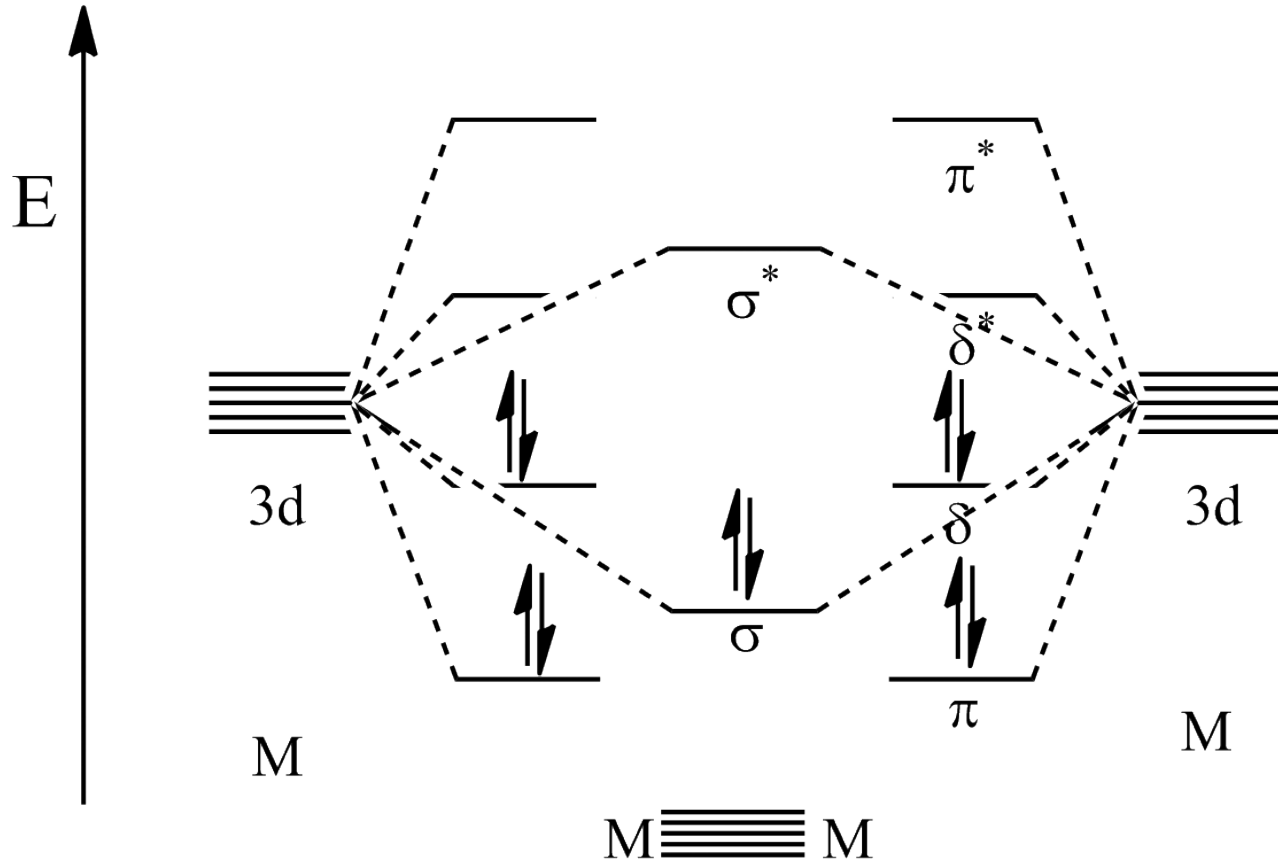
ArCrCrAr



ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ

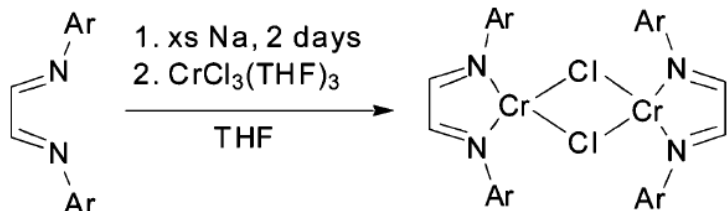


ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ



ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ

Cr-Cr = 3.431(1) Å

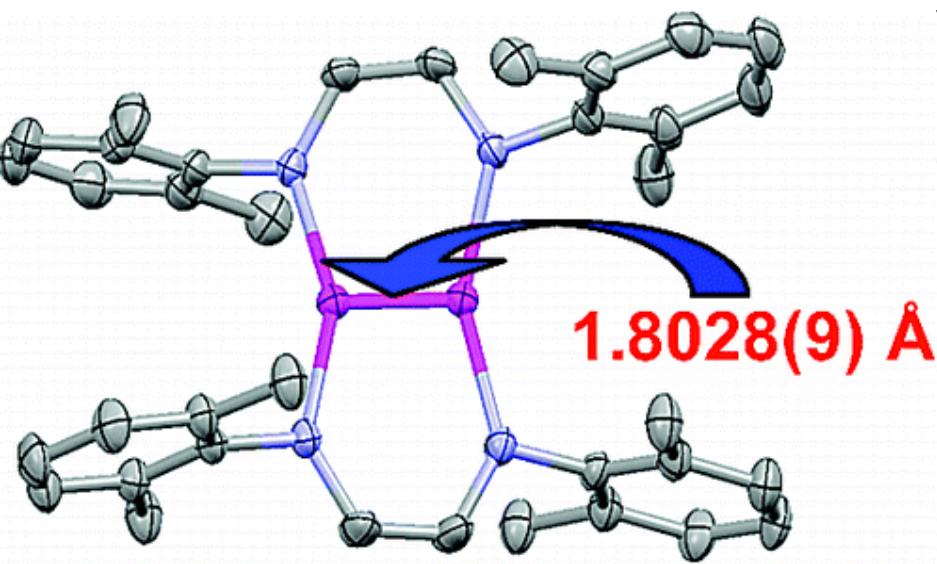
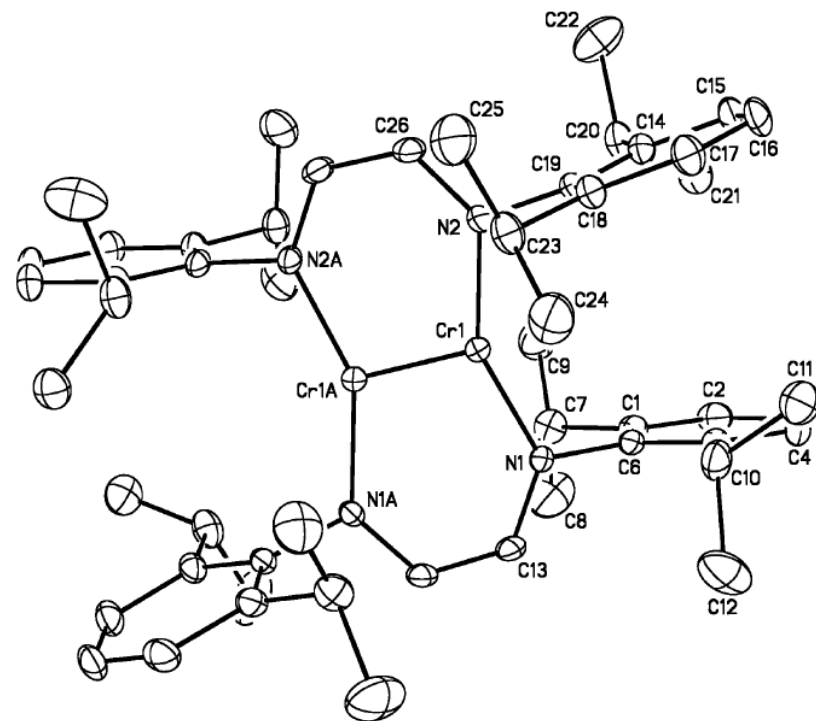


Ar = 2,6-diisopropylphenyl

1

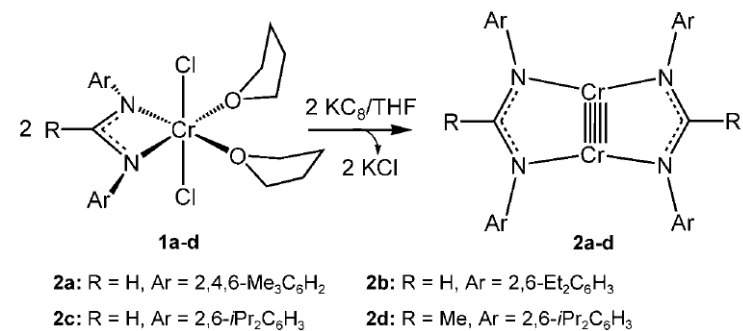
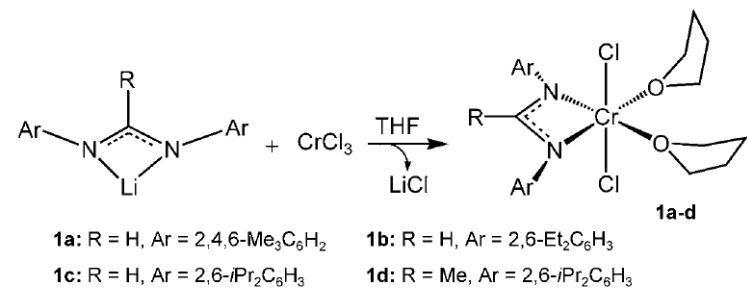
KC₈

(μ - η^{2-HL} iPr)₂Cr₂

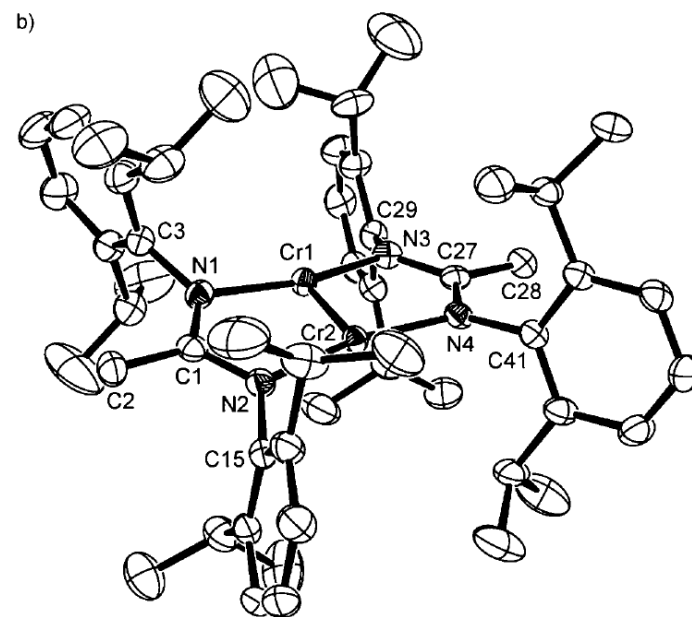
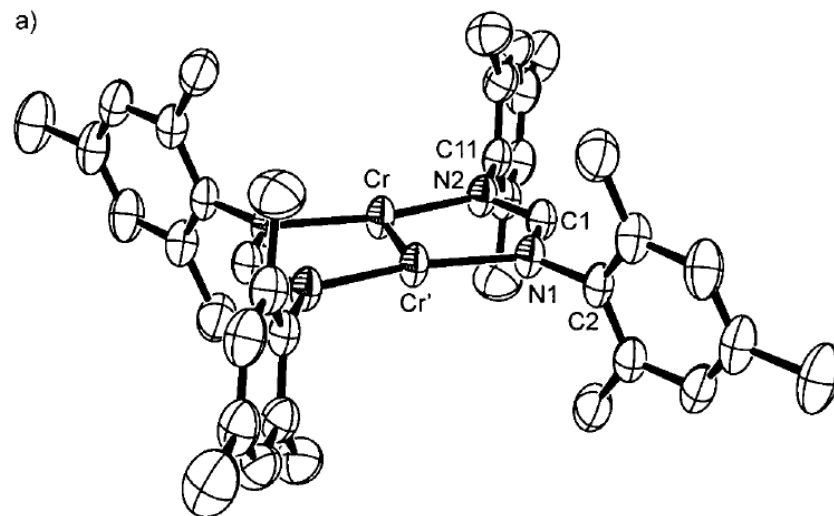


Because of the redox ambiguity of diimine and other imine containing ligands, the Cr atoms in **2** could formally be assigned as Cr(II) coordinated by dianionic enediamide ligands, Cr(I) with monoanionic ligand-centered radical ligands, or Cr(0) with neutral diimine ligands. The long C-N distances (1.373(3) and 1.362(3) Å) and short C-C distances (1.345(5) and 1.354(5) Å) are consistent with a reduced diimine ligand.

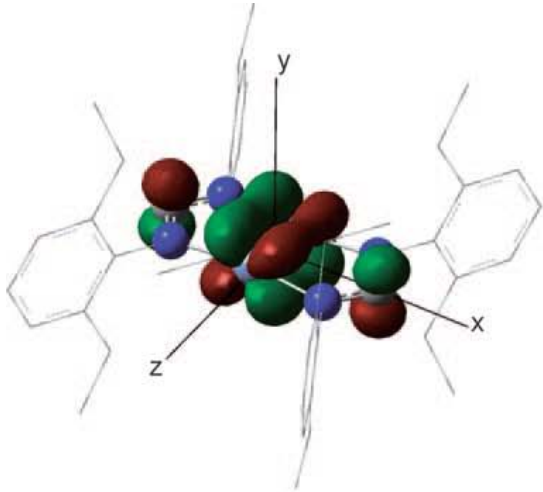
ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ



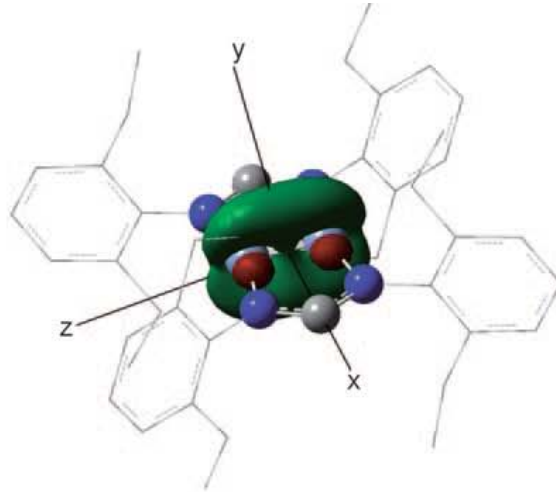
Scheme 1. Synthesis of complexes [CrCl₂(thf)₂{η²-ArNC(R)NAr}] (**1 a-d**) and [Cr₂{μ-η²-ArNC(R)NAr}]₂ (**2 a-d**).



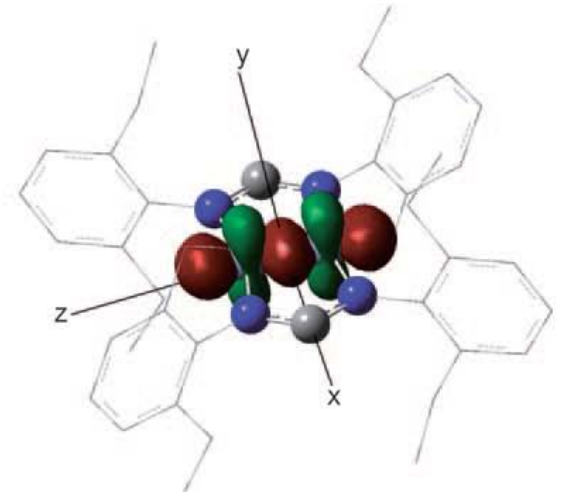
ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ



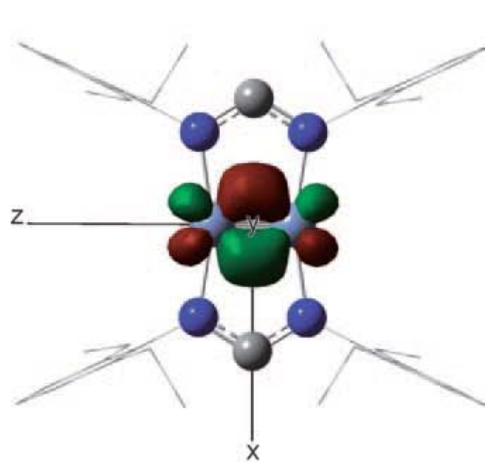
HOMO (-3.814 eV)



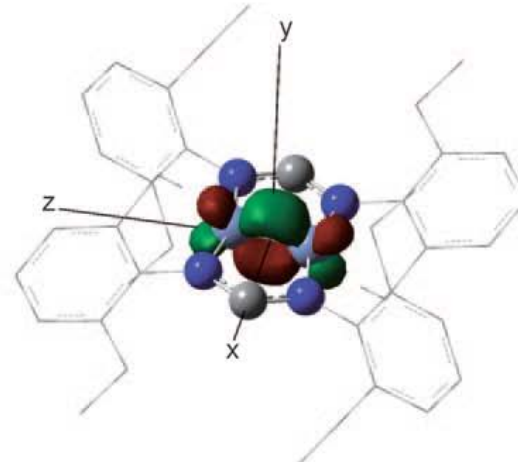
HOMO-1 (-3.980 eV)



HOMO-2 (-5.073 eV)



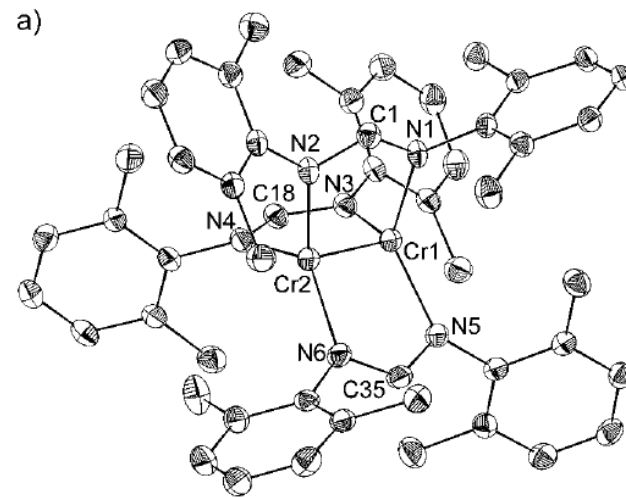
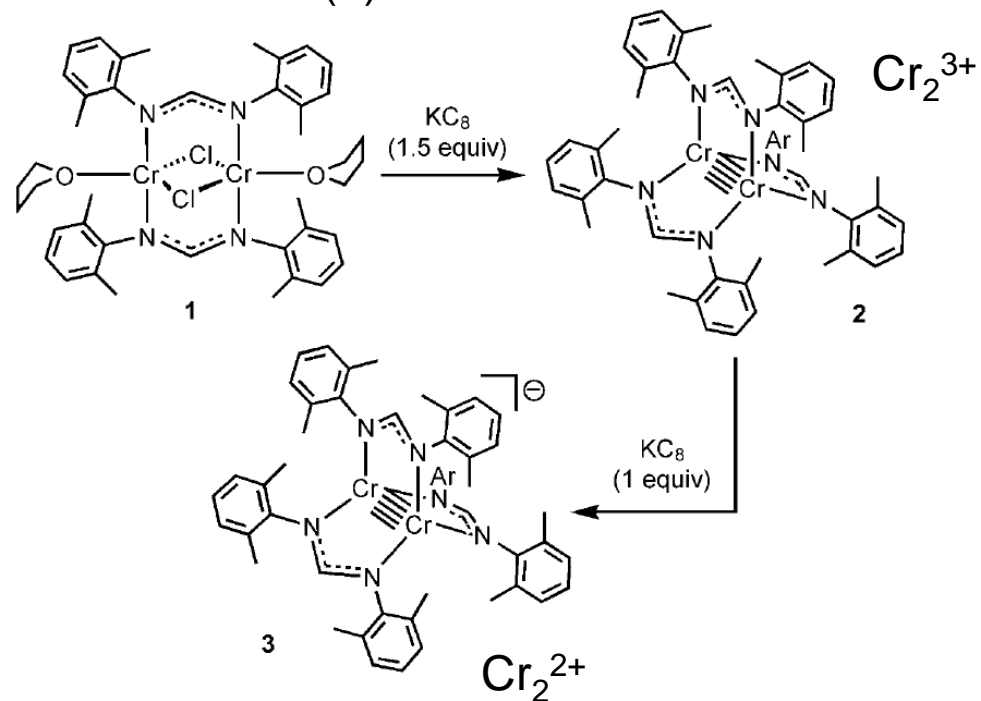
HOMO-3 (-5.507 eV)



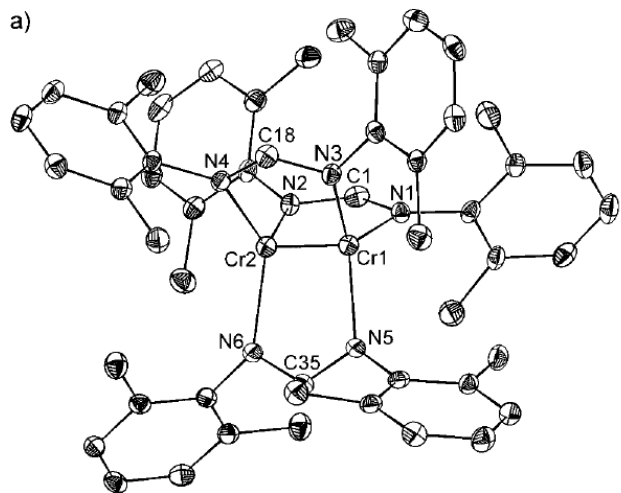
HOMO-7 (-5.695 eV)

ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ

Cr–Cr = 2.612(1) Å

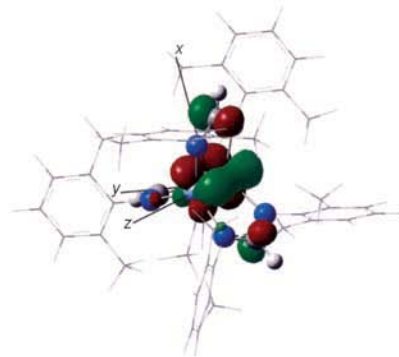


Cr–Cr = 1.8169(7) Å

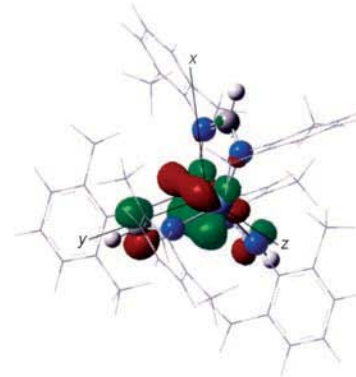


Cr–Cr = 1.7397(9) Å

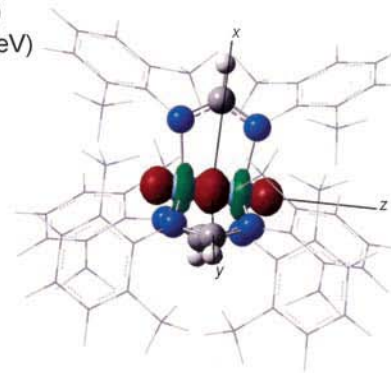
ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ



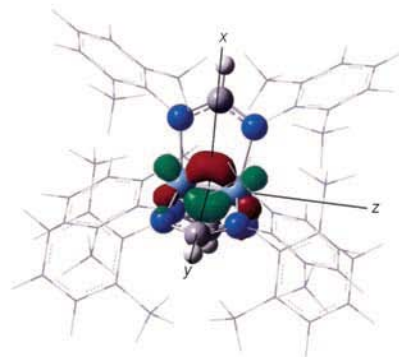
HOMO
(-0.0411 eV)



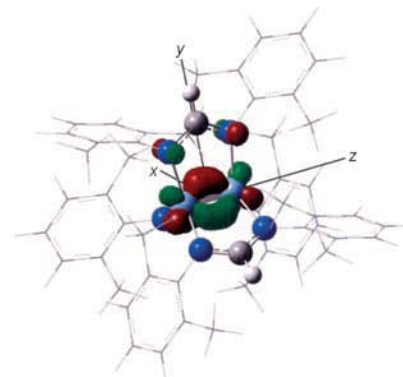
HOMO-1
(-0.0762 eV)



HOMO-2
(-1.857 eV)

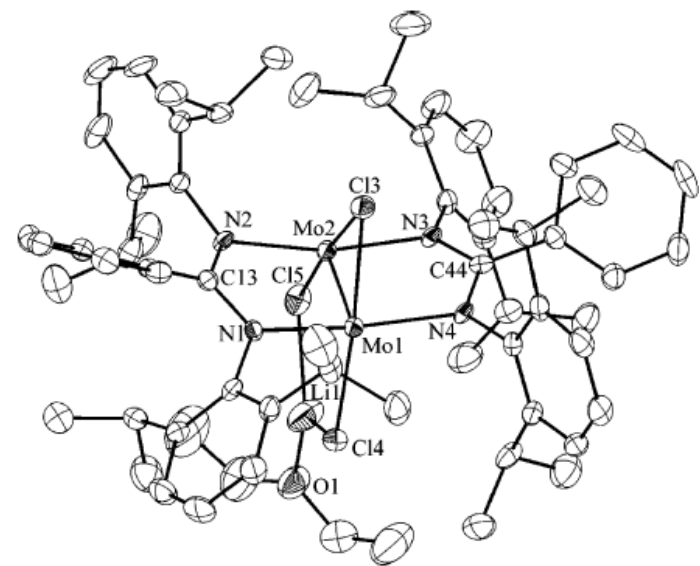
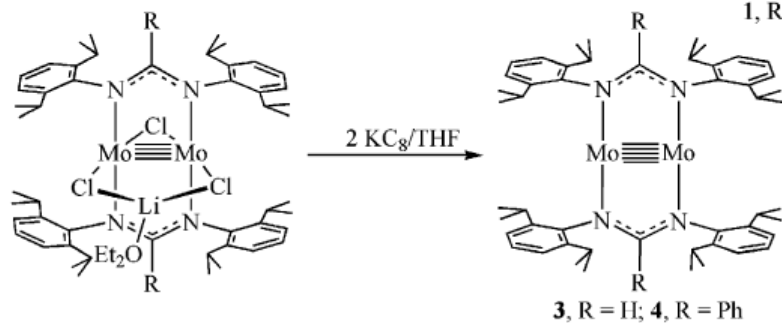
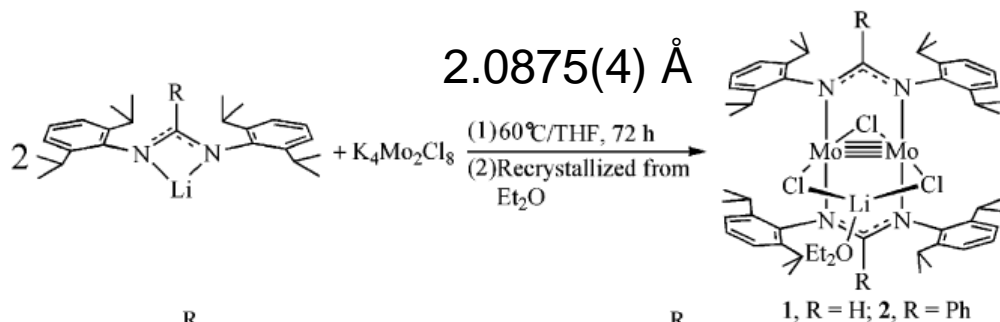


HOMO-3
(-2.241 eV)

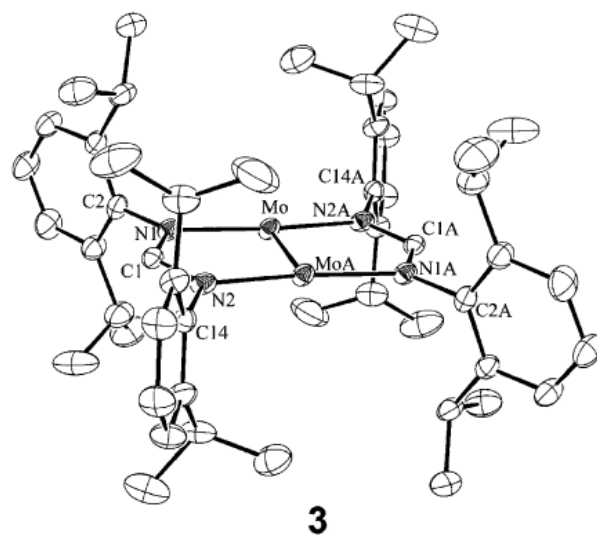


HOMO-4
(-2.246 eV)

ΠΕΝΤΑΠΛΟΣ ΔΕΣΜΟΣ

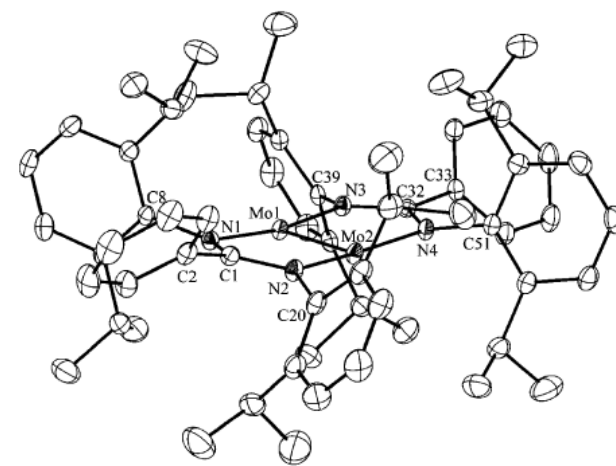


$2.0756(8) \text{ \AA}$



3

$2.0187(9) \text{ \AA}$



4

$2.0157(4) \text{ \AA}$