



Aromaticity by Any Other Name

Jeremy Henle

3-17-2015

Goals

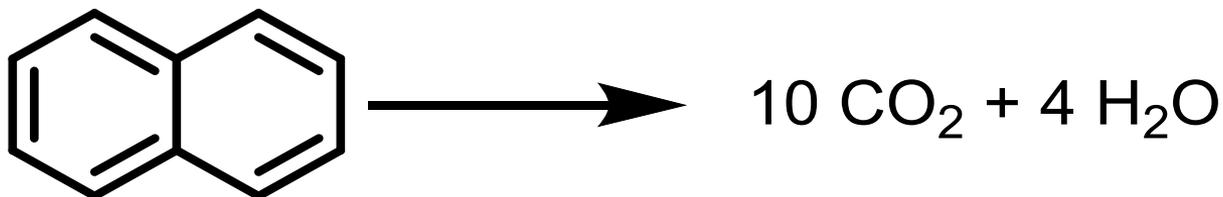
- Critically challenge your notion of “aromaticity”
- Highlight controversial claims of aromaticity in various chemical species
- Discuss what it really means to be “aromatic”

Outline

- Aromaticity Introduction
 - History
 - Modern Criteria
 - Controversy
- Cyclopropane – the origin of aromaticity
- Mobius Aromaticity – 3D Aromaticity
- Controversial Inorganic and “Fleeting” Aromaticity
- Final Thoughts

A Pchem Tale

- Dr. Rettich
 - IWU Professor of P-Chem
- Bomb calorimetry experiment: determine ΔH of combustion of naphthalene
- The question to answer is simple:
 - Is naphthalene aromatic?
- The answer....
 - Yes, but not as aromatic as benzene



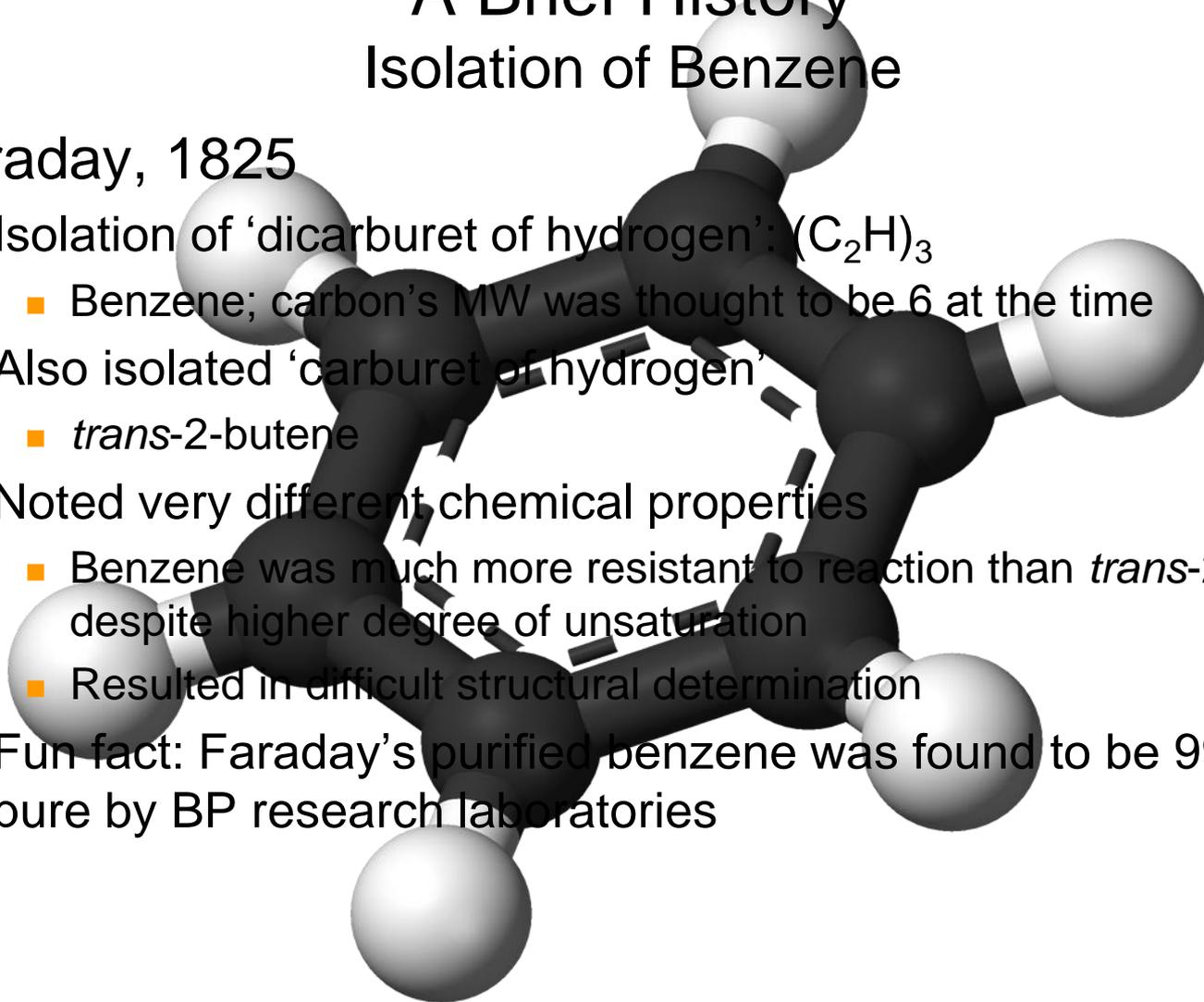
RE = 61 kcal/mol (less than twice that of benzene: ~72 kcal/mol)



A Brief History Isolation of Benzene

■ Faraday, 1825

- Isolation of 'dicarburet of hydrogen': $(C_2H)_3$
 - Benzene; carbon's MW was thought to be 6 at the time
- Also isolated 'carburet of hydrogen'
 - *trans*-2-butene
- Noted very different chemical properties
 - Benzene was much more resistant to reaction than *trans*-2-butene, despite higher degree of unsaturation
 - Resulted in difficult structural determination
- Fun fact: Faraday's purified benzene was found to be 99.7% pure by BP research laboratories



Kekule

“Father of Aromaticity”

■ 1865

- First published his structure of benzene
- Believed it to be an alternating structure of single and double bonds

■ 1872

□ R

c

□ B

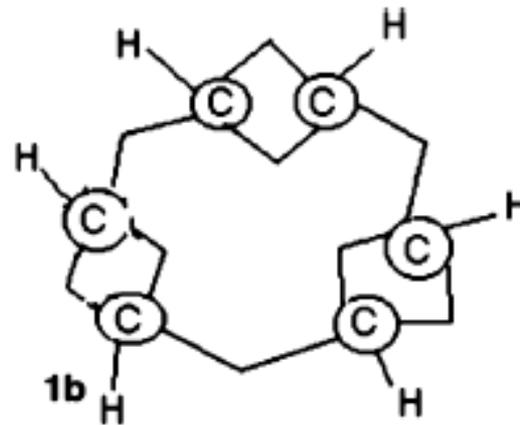
r

□ N

b



1a



1b

erved

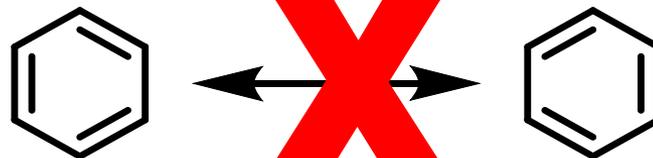
)

the ring

ation of the

, but

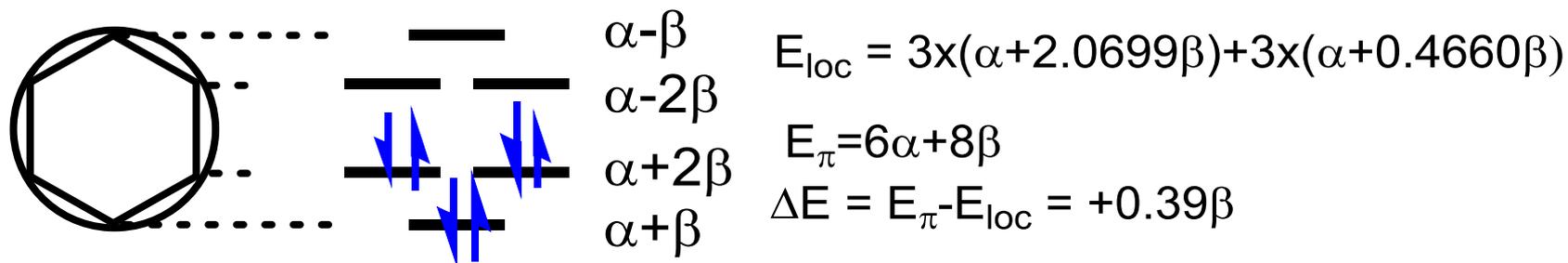
rather as a constant symmetrical structure



Huckel

$$4n+2$$

- 1925, Armit-Robinson establish the idea aromatic sextet – at least got credit
 - Crocker published the concept 1922
- 1931 – Huckel, theory of cyclic systems



Aromaticity

Modern Criteria

- Fully aromatic compounds are:

- More stable than an acyclic conjugated reference, or a saturated cyclic reference compound

- Have bond lengths between those typical of single and double bonds



c1ccccc1 + H2 >> C1CCCCC1
 $\Delta H = -28.3 \text{ kcal/mol}$

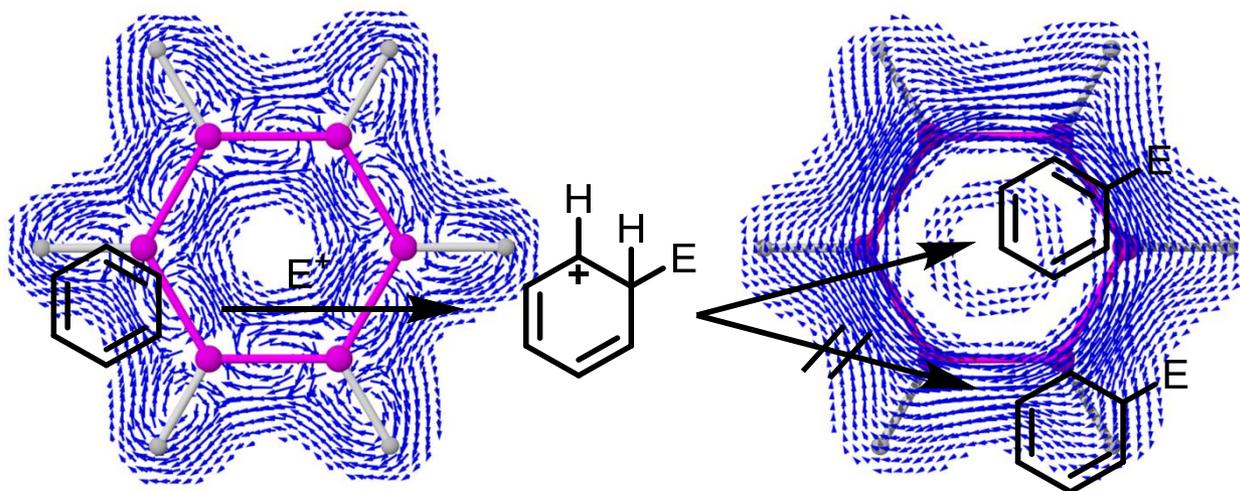
- Have a π -electron ring current that is induced when the system is exposed to external magnetic fields, leading to increased values of the magnetic susceptibility

-

(i)

“F
pr

l
e
e



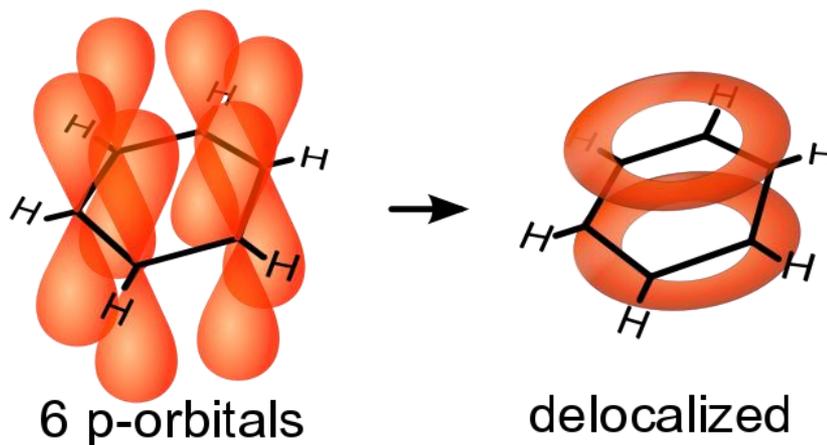
retain

these

e of

Modern Controversy

- R. Hoffman
 - Published an editorial discouraging the use of the term “aromatic” to systems that are outside the classical aromatic systems
 - Believes that attributing aromaticity to inorganic, fleeting, or high energy species is essentially ‘hype’
- Aromaticity is a “virtual” property
 - Cannot be measured experimentally



Degree of Aromaticity

How much is enough?

- In some ways, an uncomfortable concept
 - If aromaticity is a gradient, where does the “aromatic” group stop being “aromatic”?
- How can the degree of aromaticity be measured?
 - Structure, reactivity, existence of ring currents?
 - Relative stability?
 - How stable is stable enough?
 - Persistence?
 - Does the compound need to be ‘bottled’?
 - Does carbon have to be involved?
 - Do p-orbitals have to be involved?

This uncertainty forms the backbone of the question of non-traditional aromaticity

Relative Aromaticity

Attempts to Quantify Aromaticity

■ Molecular Geometry

□ Harmonic Oscillation Measure of Aromaticity (HOMA)

- Uses a normalization method to determine how close a ring is to the optimal for a fully aromatic system (must be calibrated for specific systems)
- $0 < \text{HOMA} < 1$, with 1 being fully aromatic

□ Δr – difference between longest and shortest C-C bond

- $\Delta r > 0.05$ is generally considered 'non aromatic' (benzene $\Delta r = 0 \text{ \AA}$)

■ Energetic Criteria

- Aromatic Stabilization Energy – Requires a frame of reference

■ Magnetic Criteria

□ Diamagnetic susceptibility exaltation, Λ (benzene: -13.4)

- Defined as the difference between the measured magnetic susceptibility of a compound, and a calculated value based on group additivity tables

□ Nucleus independent chemical shift (NICS) (benzene: -9.7 ppm)

- Calculates the absolute chemical shielding at the center of rings

Outline

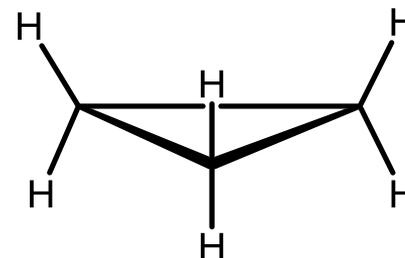
- Aromaticity Introduction
 - History
 - Modern Criteria
 - Controversy
- Cyclopropane – the origin of σ -aromaticity
- Mobius aromaticity – 3D aromaticity
- Controversial Inorganic and “Fleeting” Aromaticity
- Final Thoughts

The Confusing Case of Cyclopropane

The origin of σ -aromaticity

■ Cyclopropane features

- C-C bond length: 1.51 Å (1.53 Å in cyclohexane)
- Interior angle: 60°
- Strain energy: 27.6 kcal/mol
- Eclipsed hydrogens
- Planar ring
- Unusual reactivity

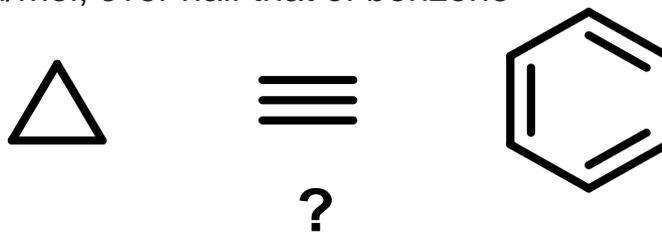


■ Dewar: Curious that the strain energy is similar to that of cyclobutane (26.2 kcal/mol)

- The geometrical constraints of cyclopropane are much larger than that of cyclobutane
- Ring strain per CH₂ unit (using cyclobutane as an analogy) should be ~21 kcal/mol, giving a total expected strain energy of ~63 kcal/mol

■ Dewar reasons that the reduced ring strain energy comes from σ -delocalization, a σ -aromatic system

- If true, ASE ~ 26 kcal/mol, over half that of benzene

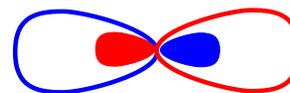


The Confusing Case of Cyclopropane

The origin of σ -aromaticity

- Dewar: σ -conjugation

- Consider an sp hybridized carbon



$$\psi_1 = 1/\sqrt{2}(s-p) \quad \psi_2 = 1/\sqrt{2}(s+p)$$

- Is there interaction between these orthogonal AOs?

- To determine this, one must look at the resonance integral between them

$$\beta = \int \varphi_1 H \varphi_2 d\tau = \left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{\sqrt{2}}\right) \int (s+p)H(s-p)d\tau$$

$$\beta = \left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{\sqrt{2}}\right) \left\{ \int sHs d\tau + \int sHp d\tau + \int pHs d\tau + \int pHp d\tau \right\}$$

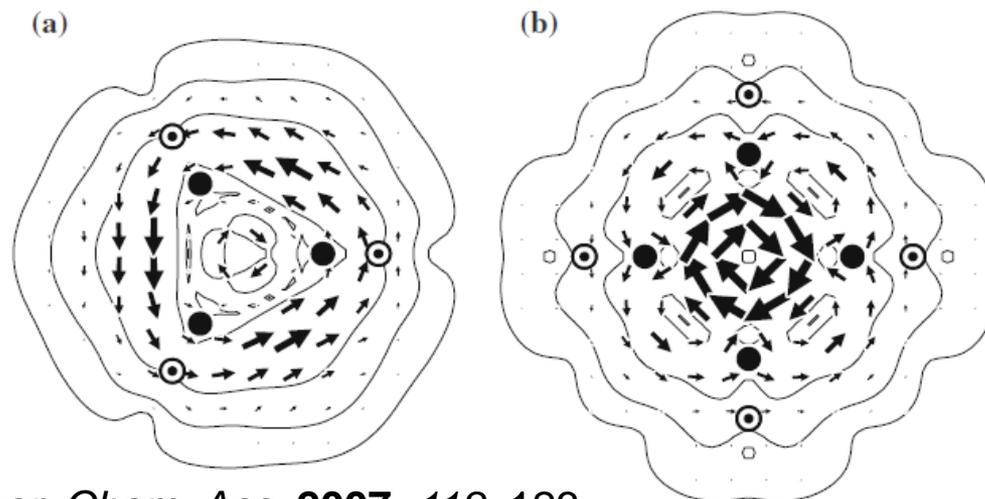
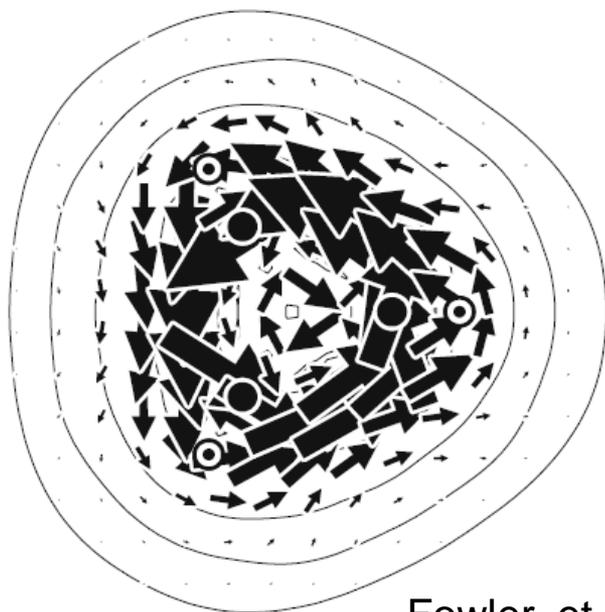
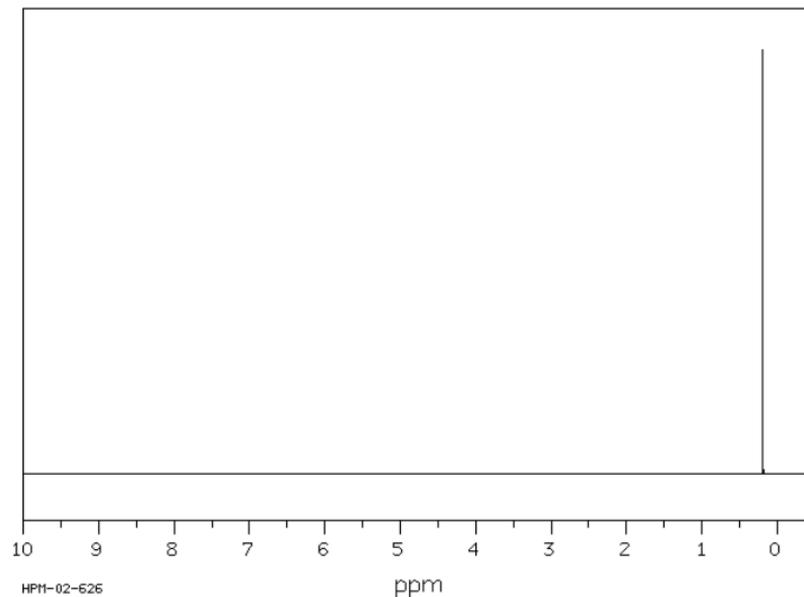
$$\beta = \left(\frac{1}{2}\right) (E_s - E_p)$$

- For carbon, $(1/2)(E_s - E_p) \sim 100$ kcal/mol
- Even in the case of sp^3 carbon, the resonance integral would be greater than that attributed to the $2p\pi$ - $2p\pi$ integral in a conjugated hydrocarbon

The Confusing Case of Cyclopropane

NMR evidence of σ -aromaticity

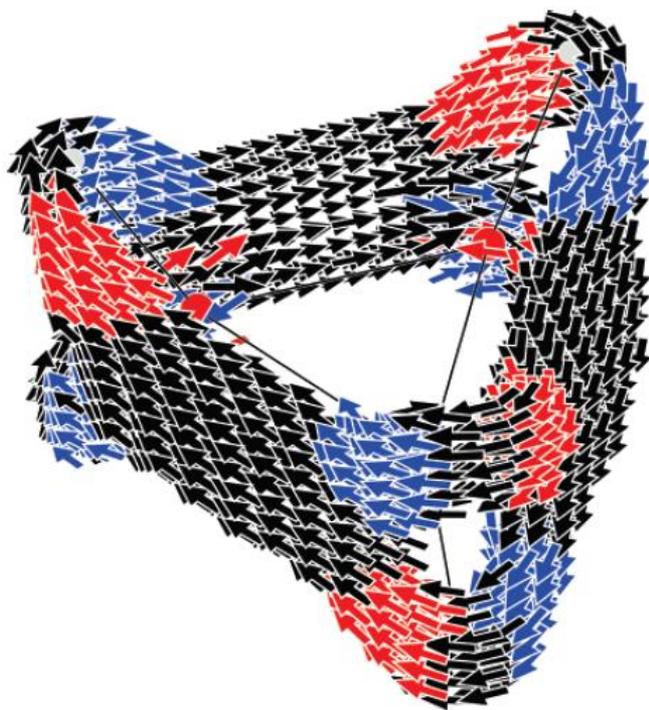
- Upfield shift of the hydrogens indicate anisotropic ring current
- NICS(1) values:
 - Cyclopropane: -8.9 ppm
 - Benzene: -10.2 ppm
 - Cyclobutane: +1.2 ppm
- Ring current model



The Confusing Case of Cyclopropane

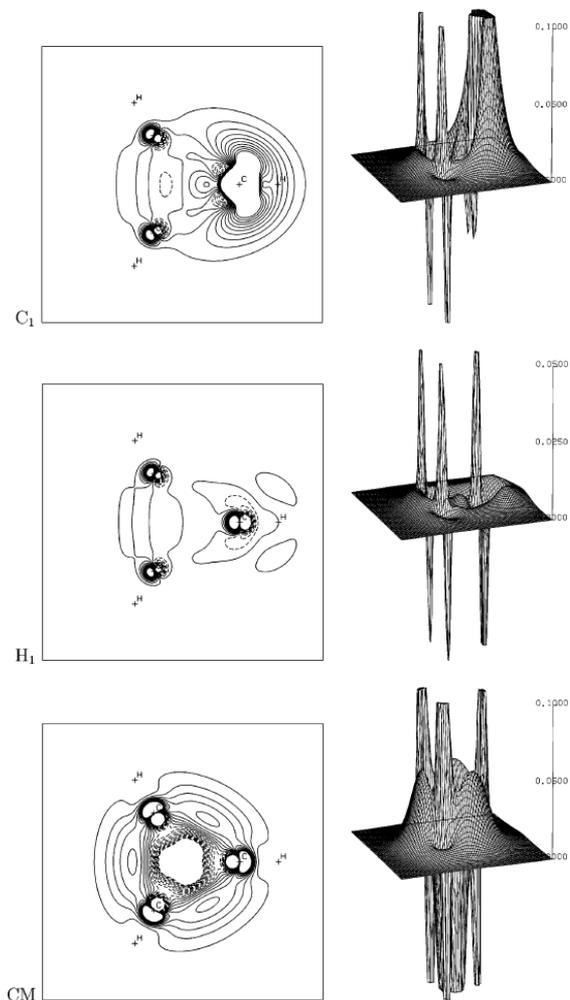
Is invoking σ -aromaticity necessary?

- Conflicting NMR computational evidence



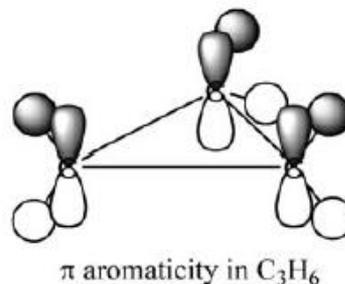
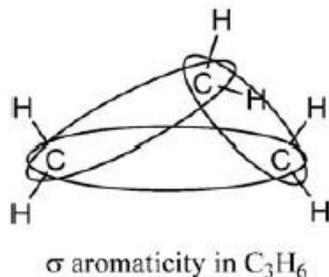
Relatively weak ring current follows the perimeter of the carbon skeleton

Ring current bifurcates at the carbons, indicating C-H localized anisotropy



The Confusing Case of Cyclopropane

Deconvoluting Stabilization Energies



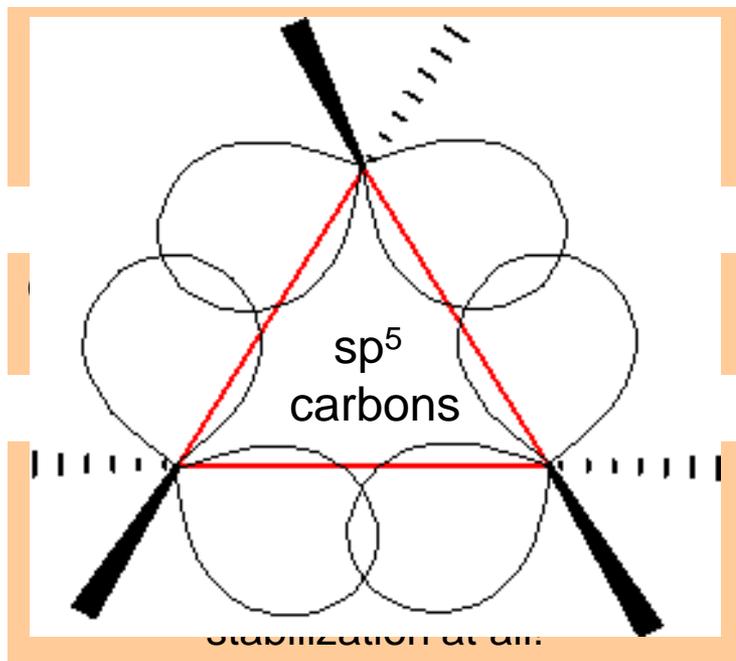
Species		X = C	
		6-31G(d)	cc-pVDZ
X_3H_6	RE^σ	12.7	12.5
	RE^π	8.6	10.2
	$RE^{\sigma+\pi}$	21.2	22.7
X_3H_8	RE^σ	7.9	9.0
	RE^π	6.8	8.4
	$RE^{\sigma+\pi}$	14.7	17.3
X_4H_{10}	RE^σ	11.6	13.2
	RE^π	10.4	12.9
	$RE^{\sigma+\pi}$	21.8	25.9
X_4H_8	RE^σ	13.6	14.8
	RE^π	10.3	12.7
	$RE^{\sigma+\pi}$	23.8	27.5
X_5H_{12}	RE^σ	15.2	17.3
	RE^π	13.9	17.3
	$RE^{\sigma+\pi}$	29.0	34.4

Species		X = C	
		6-31G(d)	cc-pVDZ
X_3H_6	$ECRE1^\sigma$	4.8	3.5
	$ECRE1^\pi$	1.8	1.8
	$ECRE1^{\sigma+\pi}$	6.5	5.4
	$ECRE2^\sigma$	1.1	-0.7
X_4H_8	$ECRE2^\pi$	-1.8	-2.7
	$ECRE2^{\sigma+\pi}$	-0.6	-3.2
	$ECRE1^\sigma$	2.0	1.6
	$ECRE1^\pi$	-0.1	-0.2
	$ECRE1^{\sigma+\pi}$	2.0	1.6
	$ECRE2^\sigma$	-1.6	-2.5
	$ECRE2^\pi$	-3.6	-4.6
	$ECRE2^{\sigma+\pi}$	-5.2	-6.9

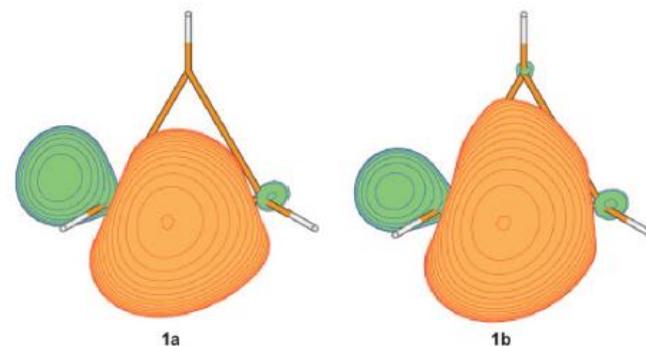
The extra cyclic resonance energy of cyclopropane is only 5.4 kcal/mol

The Confusing Case of Cyclopropane

Where does the stabilization come from?



Schleyer and co-workers determined that the “bent-bond” model could be further elaborated.



Bond-distorted orbitals: green
Overlap-enhanced orbitals: orange

The BDO bends out by 25° , giving each carbon essentially sp^3 hybridization negating the angle strain.

Summary

Aromaticity in cyclopropane

- Signs of aromaticity in cyclopropane
 - Appears to have unusual stabilization with respect to expected ring strain
 - Observable ring current
 - Planar cyclic structure
 - Negative NICS
 - Unusual chemical reactivity
- However, further theoretical investigations indicate that cyclic RE in cyclopropane is not larger than hyperconjugative stabilization in the acyclic structure
 - Thus a major criteria of aromaticity is missing
- Aromatic?
 - Schleyer believes not. However, it is interesting to note that Schleyer believes the existence of σ -aromaticity should not be doubted in “other” cases.
 - Wikipedia still cites cyclopropane as having 11.3 kcal/mol in σ -aromaticity

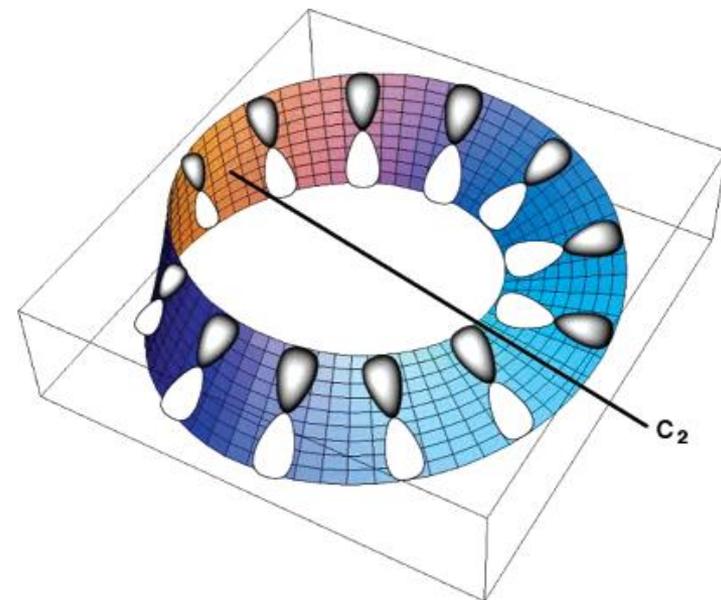
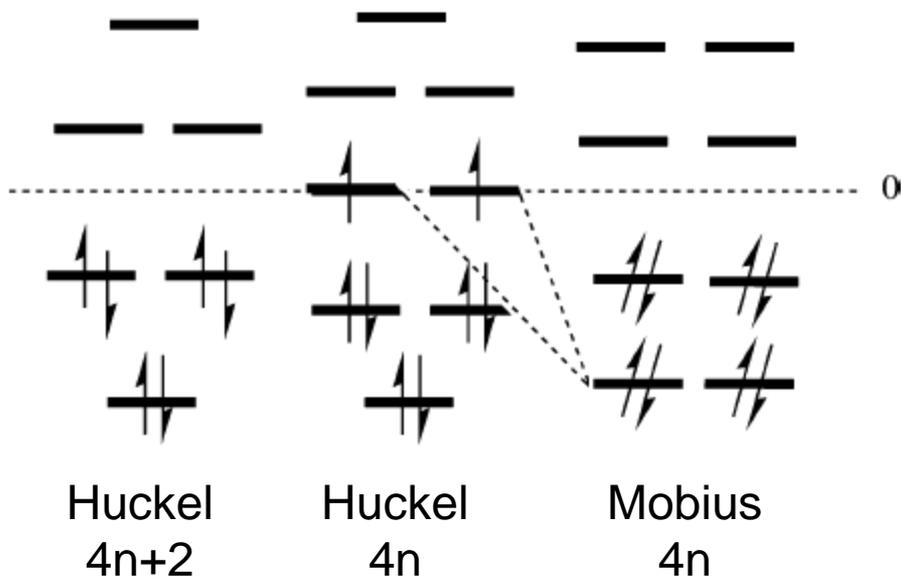
Outline

- Aromaticity Introduction
 - History
 - Modern Criteria
 - Controversy
- Cyclopropane – the origin of σ -aromaticity
- **Mobius aromaticity – 3D aromaticity**
- Controversial Inorganic and “Fleeting” Aromaticity
- Final Thoughts

Aromaticity in 3D

Mobius Aromaticity

- Heilbronner in 1964 predicted $4n$ Mobius species would be closed-shell
 - Believed $n \geq 20$ would be required to overcome ring strain



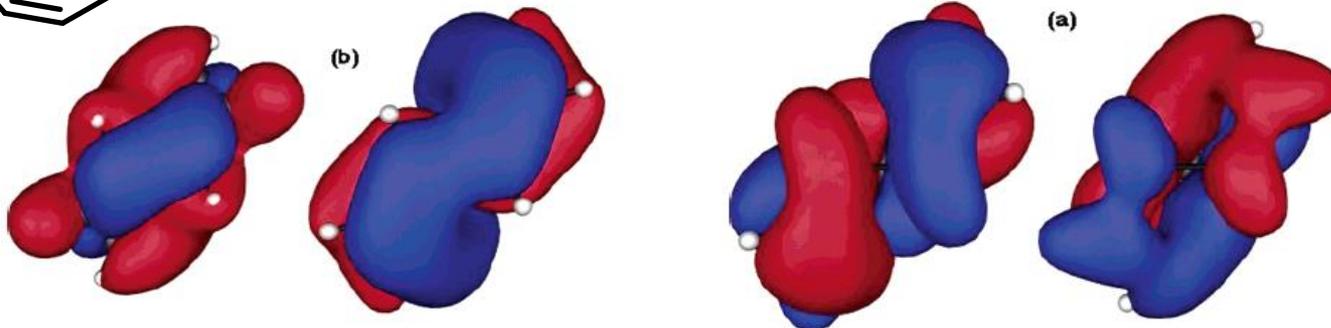
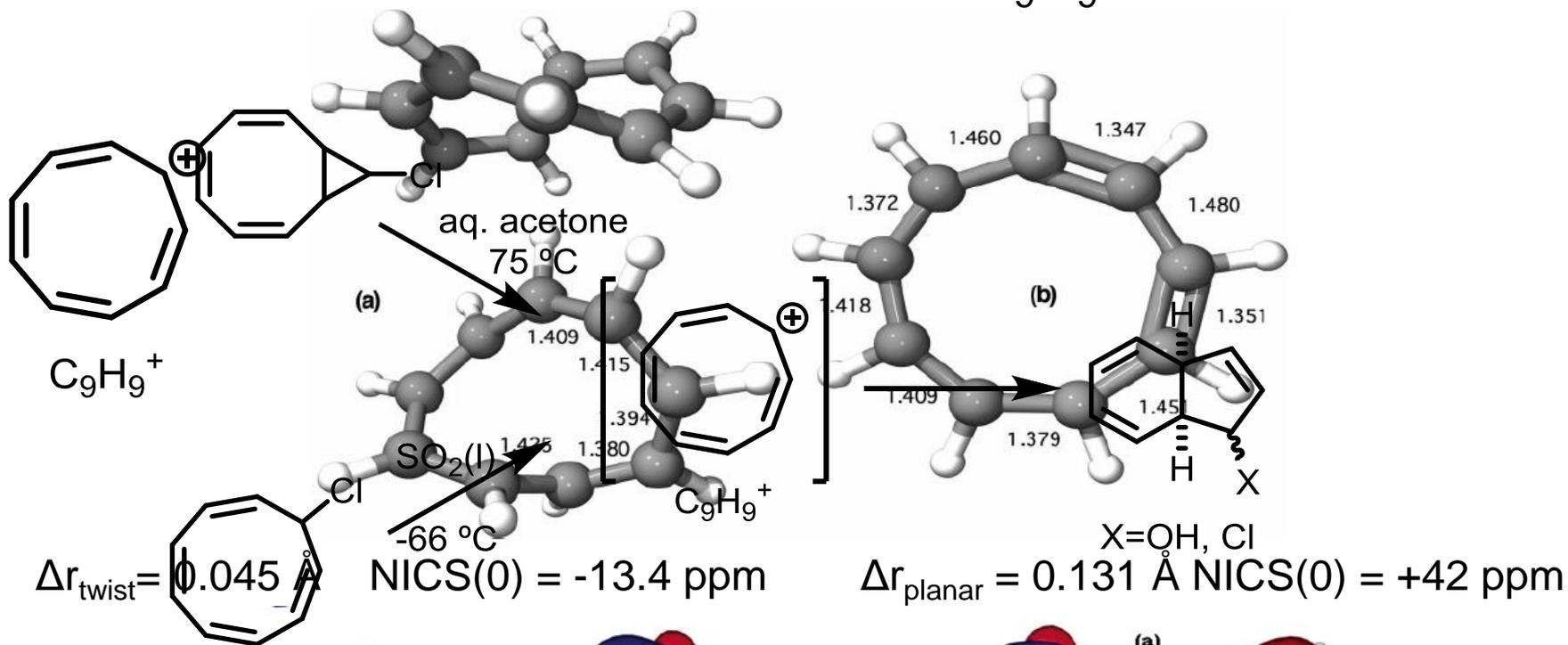
180° half-twist results in orbital degeneracy resulting in 4 doubly occupied π -orbitals, albeit at increased energy levels

Measuring Mobius Aromaticity

- Bond Lengths
 - Maximum difference between bond lengths (Δr) $\leq 0.5 \text{ \AA}$
- HOMA
 - < 1.0 indicates aromaticity
- ASE
 - $\sim 1.5\text{-}3.0 \text{ kcal/mol}$ per ring carbon
 - Not systematically evaluated for highly-nonplanar systems
- NICS(0)
 - -10 to -15 ppm

Mobius Aromaticity

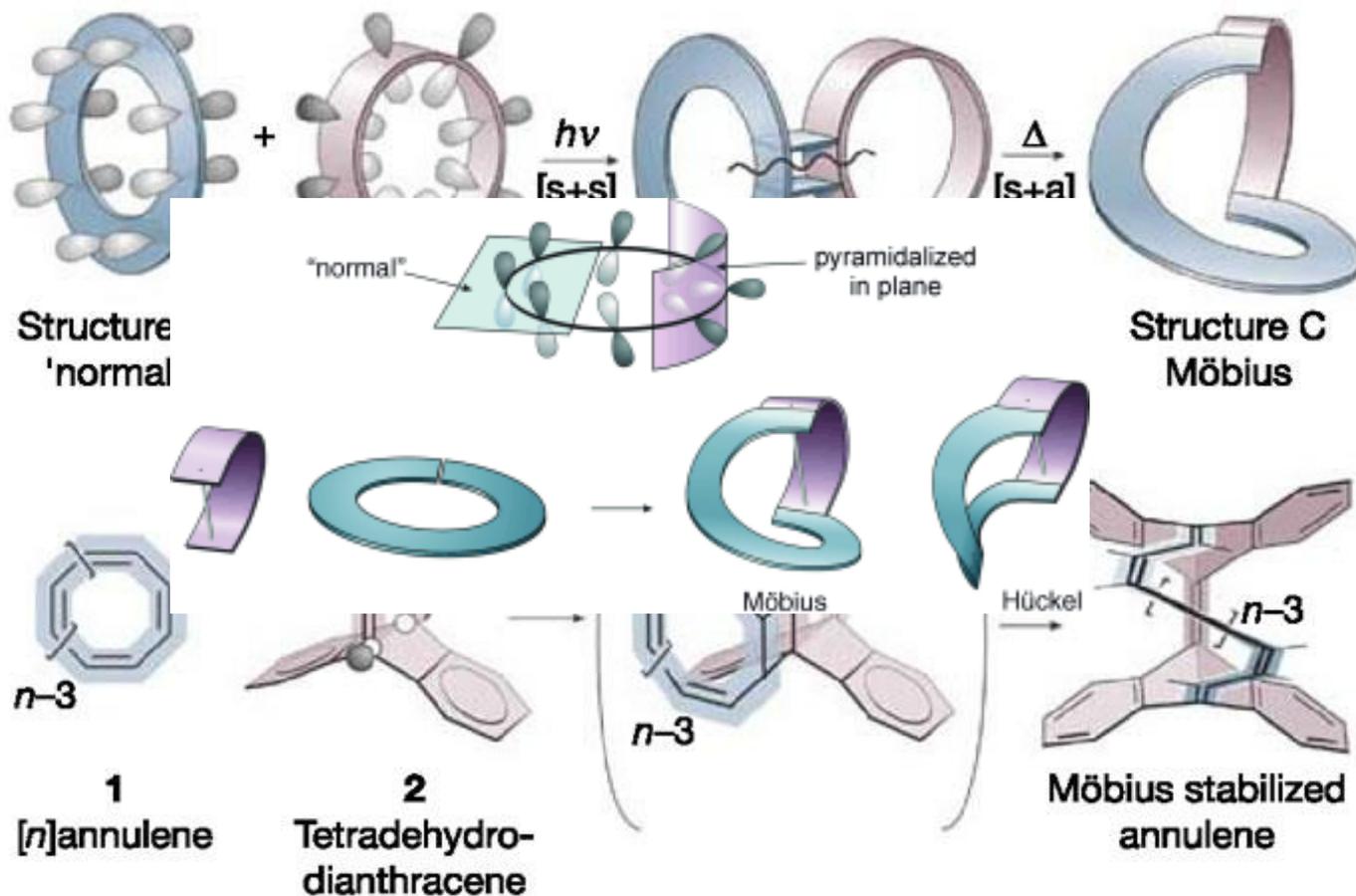
Theoretical Studies of $C_9H_9^+$



B3LYP/6-311G(d,p)

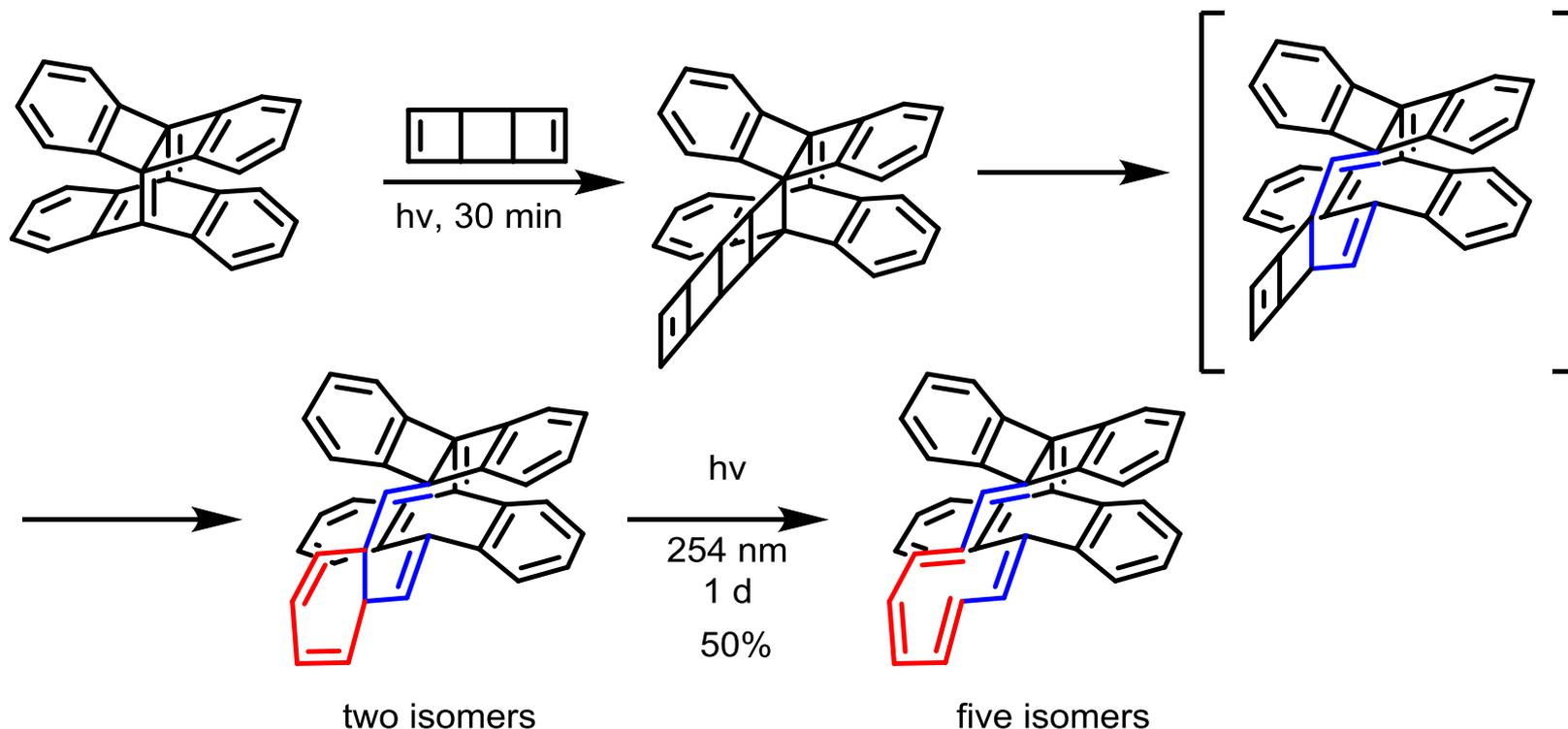
Schleyer, et al. *ACIE*, 1998, 37, 2395.

Synthesis of the First Möbius-Aromatic Compound Strategy



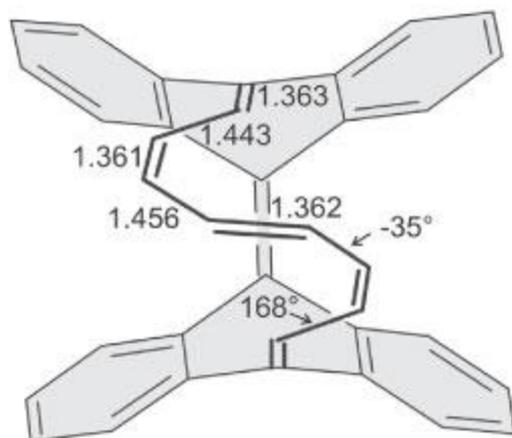
Attempt to stabilize the möbius structure of a [16]annulene using a rigid backbone

Synthesis of the First Mobius Aromatic Compound

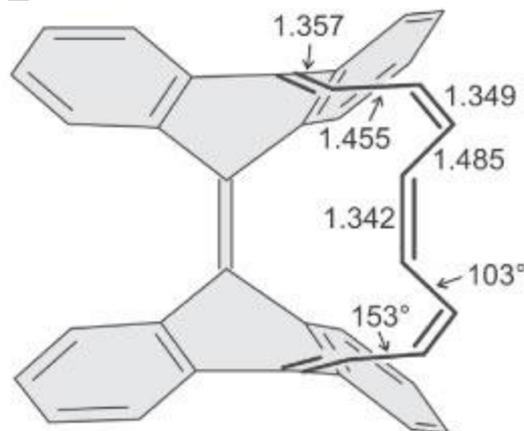


Two "Mobius" isomers (C_1 and C_2 symmetry)
Only C_2 Mobius isomer had sufficient conjugation
Also one Huckel isomer (C_s symmetric)

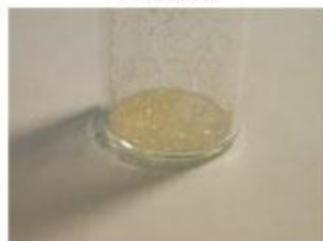
Characterization of C₂-Mobius Hydrocarbon



C₂
Möbius



C_s
Hückel



These are the structures and bond lengths presented in the paper.

Bond lengths/angles are calculated even though they took X-Ray

Aromaticity Criteria	Mobius	Huckel
HOMA (bridge)	0.50 (moderate)	0.05
HOMA (whole)	0.35 (moderate)	0.17
Δr (bridge)	0.095 Å (>0.05 Å crit.)	0.143 Å
RE (calculated, ISE)	4.04 kcal/mol	-2.22 kcal/mol

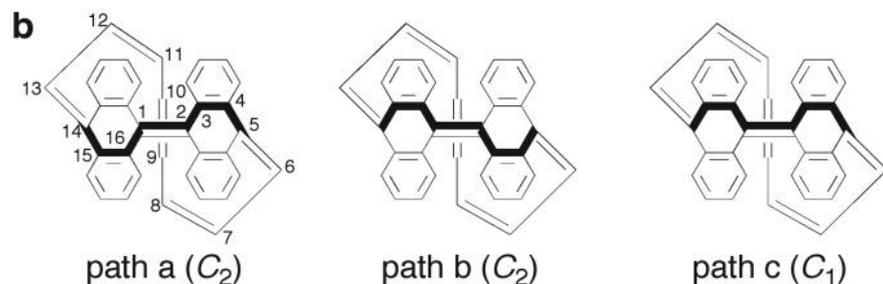
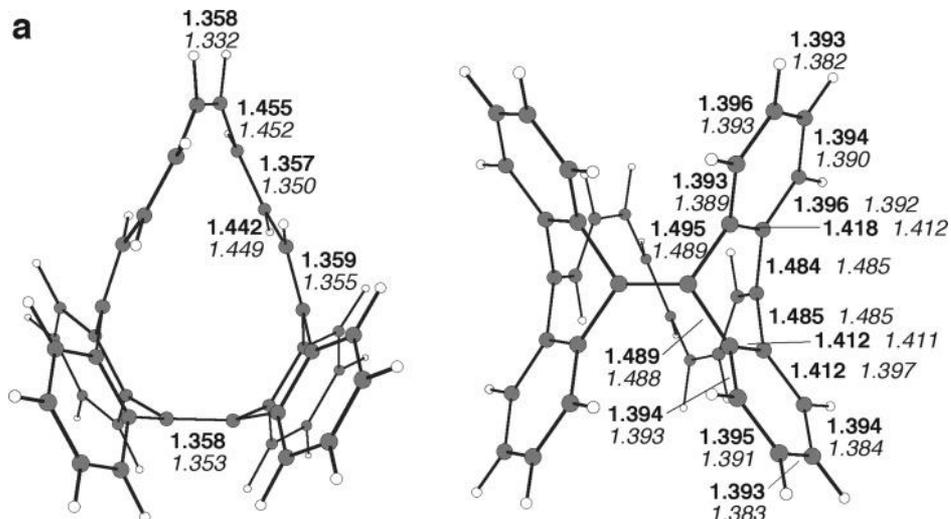
Is Mobius-C₂ Actually Aromatic?

Numbers in italics are bond lengths from the actual crystal data:

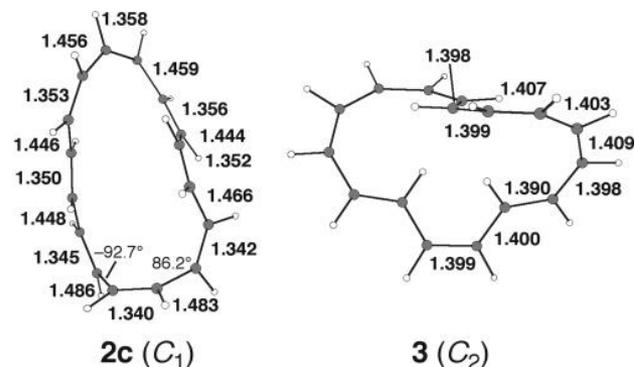
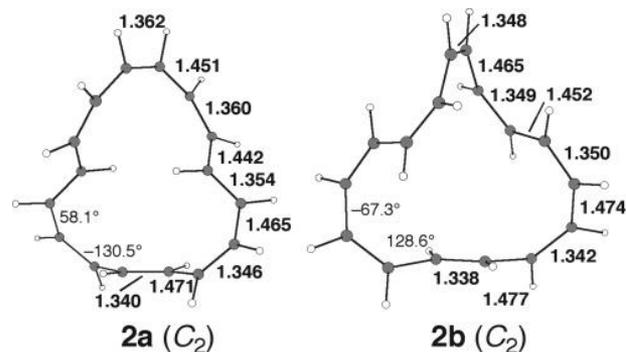
$$\Delta r = 0.139 \text{ (xray)} \text{ to } 0.157 \text{ (DFT)} \text{ \AA}$$

(heavily localized)

$$\text{NICS}(0) = -3.4 \text{ ppm (non-ar)}$$

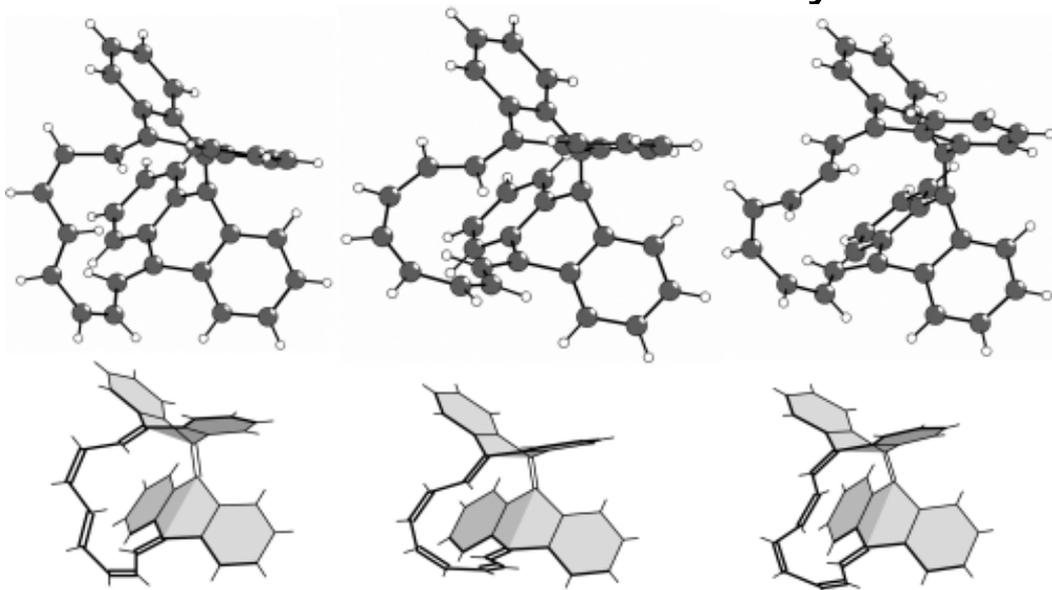


Path a matches exptl X-ray data



Möbius Aromaticity

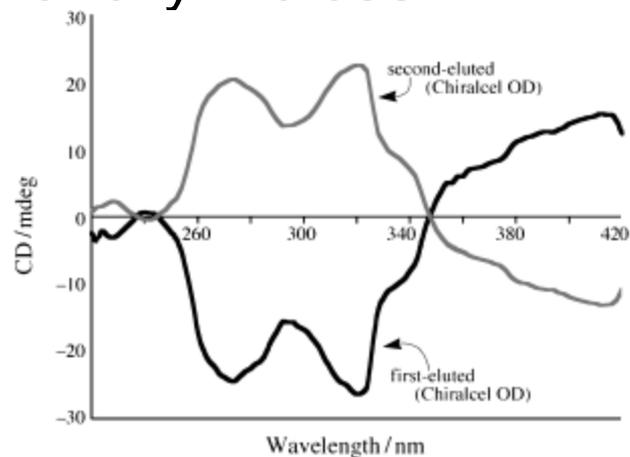
Statistical Analysis of Aromaticity Indices



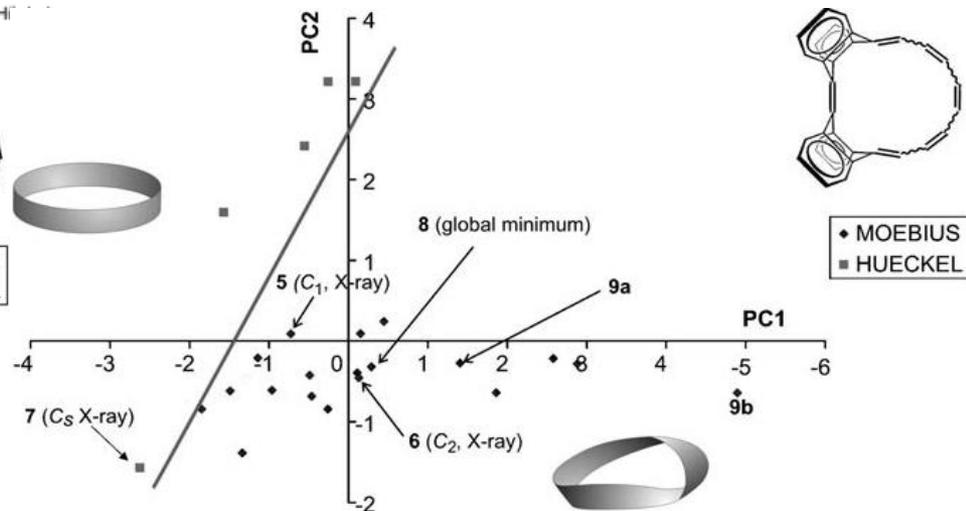
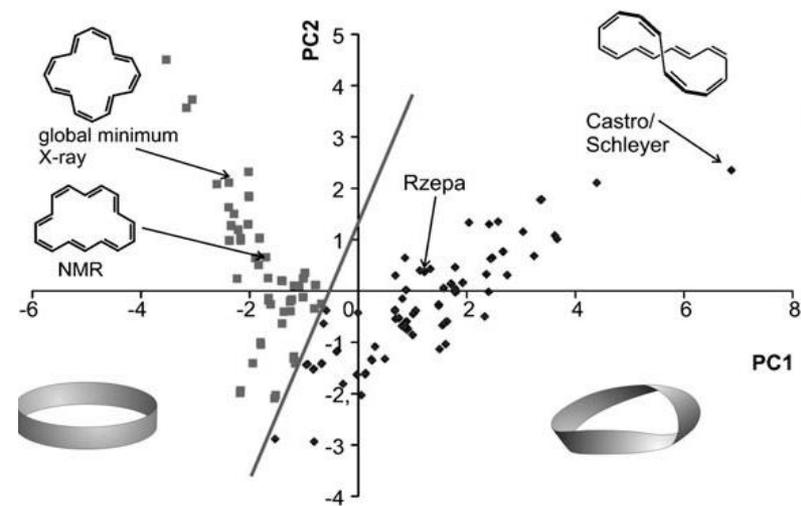
5 anti-tZtEcZt C_1 Möbius

6 anti-tZcZcZt C_2 Möbius

7 syn-tZtZtZt C_8 Hückel



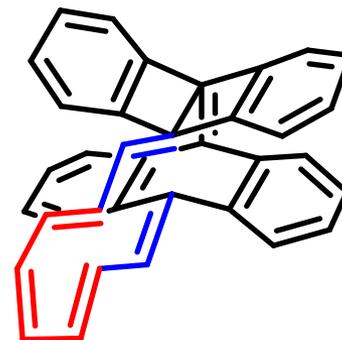
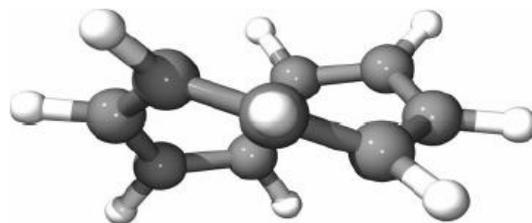
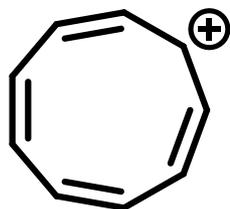
Able to separate enantiomers of Möbius compound 6



Mobius Aromaticity Summary

- Mobius topology is attainable

- Transition states
- Large annulenes
- Porphyrins

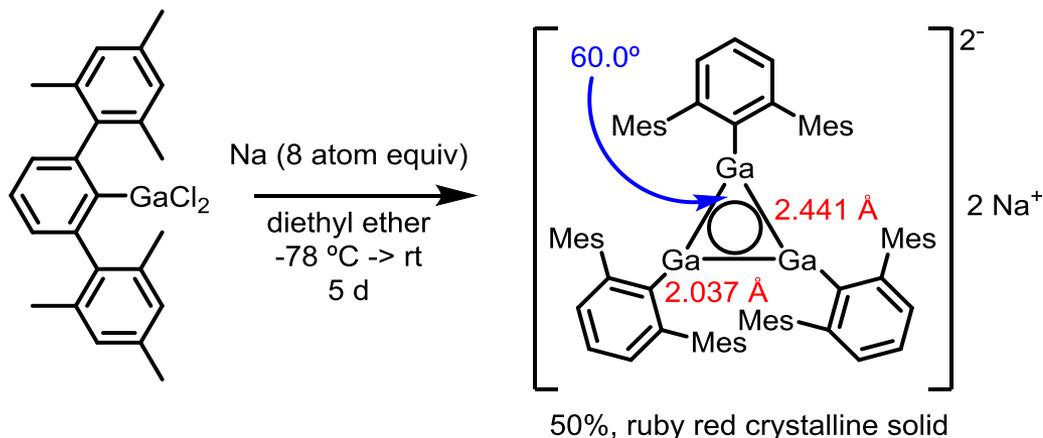


- Aromatic Mobius stabilization is hard to verify
- More definitive Mobius Aromatics have been formed in large porphyrin systems
 - Can show a switch in Huckel/Mobius topology

Outline

- Aromaticity Introduction
 - History
 - Modern Criteria
 - Controversy
- Cyclopropane – the origin of σ -aromaticity
- Mobius aromaticity – 3D aromaticity
- Controversial Inorganic and “Fleeting” Aromaticity
- Final Thoughts

All-Metal Aromaticity Cyclogallane



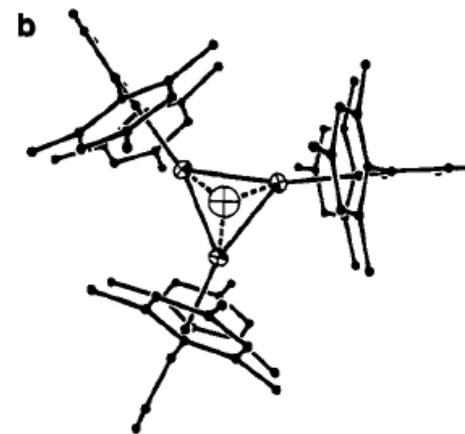
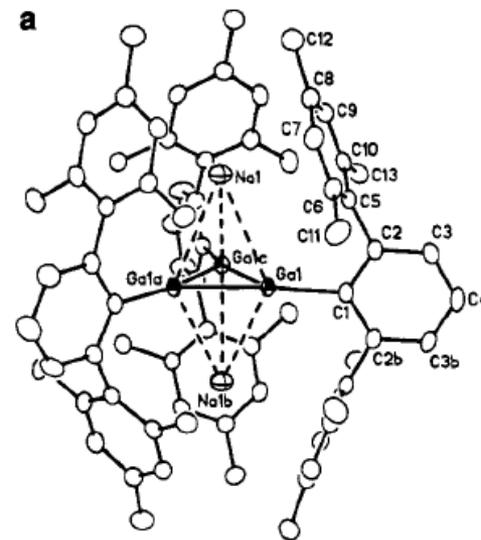
Reference bond lengths:

Ga-Ga metal: 2.70 Å

Ga=Ga: 2.343 Å (from [(Trip)₂GaGa(Trip)₂]⁺)

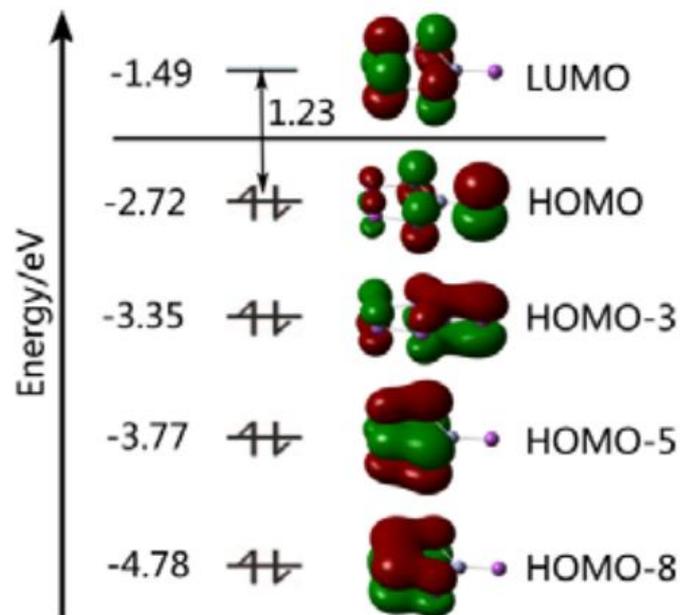
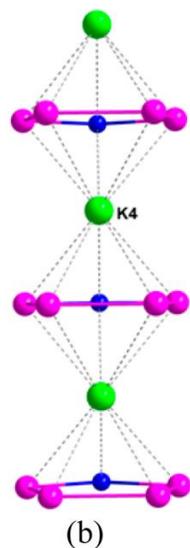
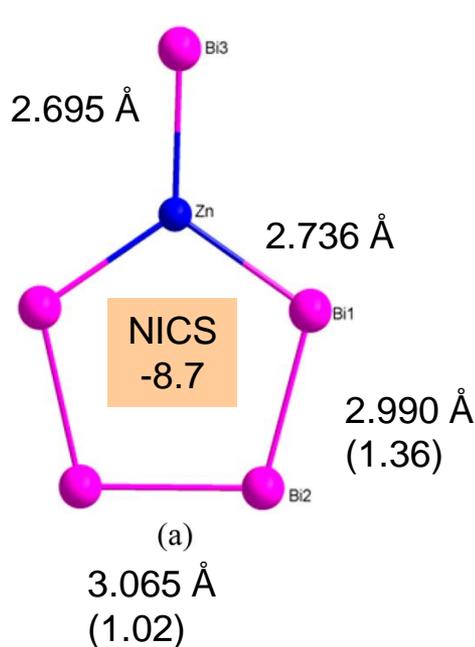
The authors reason that the Na atoms donate one electron into the unoccupied p orbitals of the sp² hybridized cyclogallane, giving 2 π-delocalized electrons, satisfying the Huckel rule.

Aromatic?



[ZnBi₄³⁻] An Aromatic Inorganic Heterocycle

- K₆ZnBi₅: Isolable, silvery grey crystalline solid.



Average Bond Lengths
 Bi-Bi: 3.206 Å
 Bi=Bi: 2.83 Å
 Zn-Bi: 2.85 Å

Negative NICS
 Intermediate bond orders
 Planar geometry
 Delocalized π-system
 Aromatic?

Detecting “Fleeting” Aromatic Species

Generation

- Chemical Reactions in the gas phase or “molecular beam” generate small amounts of high energy species

Characterization

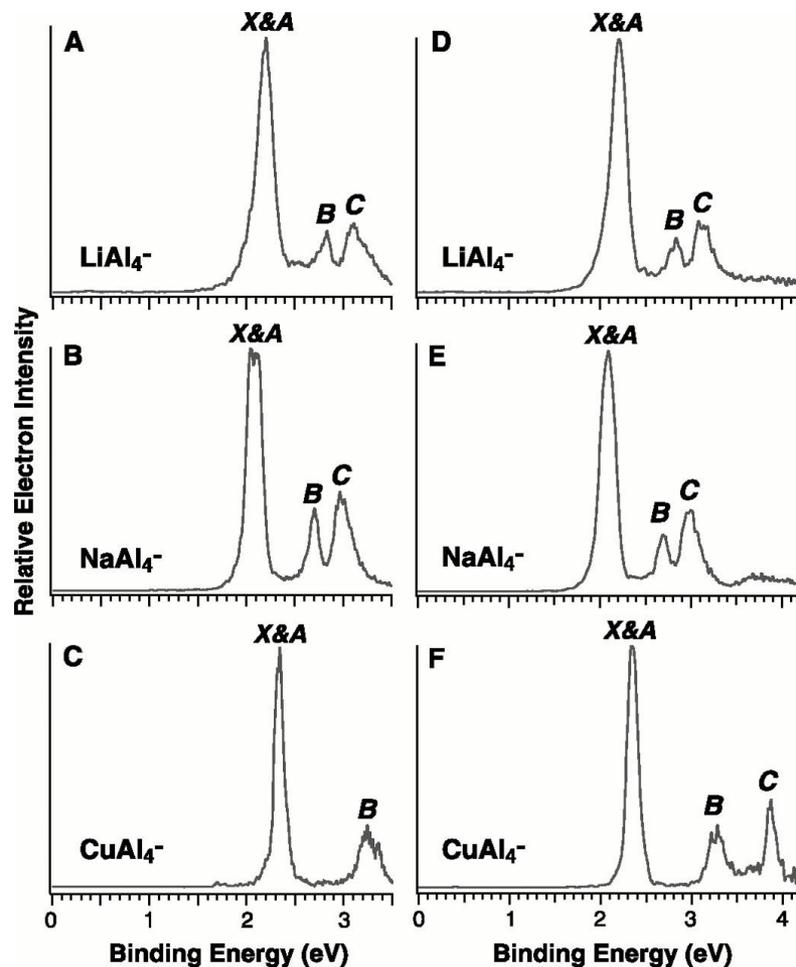
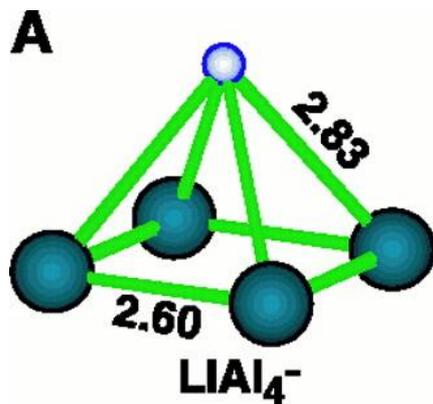
- Characterized by MS and photoelectron spectra

Confirmation

- Theoretical studies to match hypothetical structure with photoelectron spectra

Square Planar Aluminum Clusters

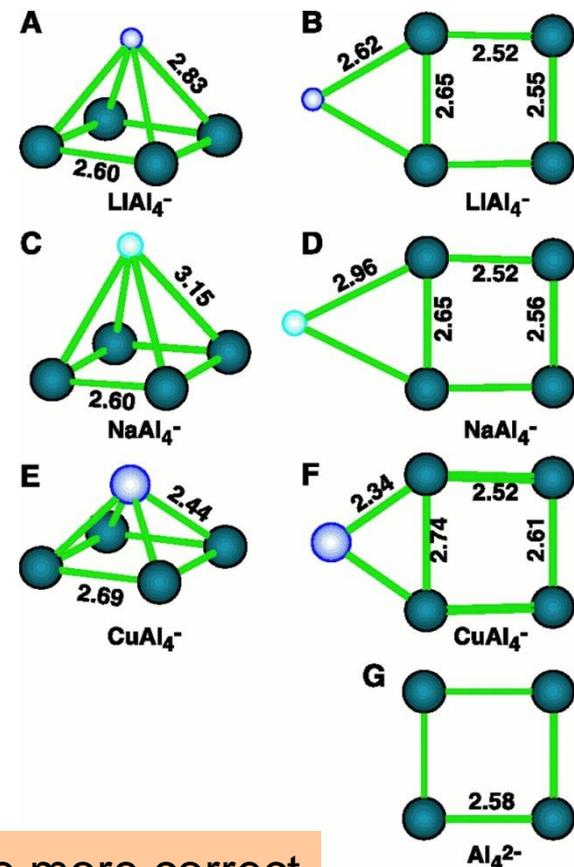
- Generated using a laser ionization source
- Characterized by MS
- Electronic structure characterized by photoelectron spectroscopy



Square Planar Aluminum Clusters

Computational Conformation of Structure

Observed features	VDE (exp.)	Square pyramid		Fully planar	
		MO	VDE (theo.)*	MO	VDE (theo.)*
			<i>LiAl₄⁻</i>		
X	2.15 ± 0.06	3a ₁	2.09 (0.86)	4a ₁	1.96 (0.86)
A	2.20 ± 0.06	1b ₁	2.17 (0.85)	1b ₁	1.98 (0.86)
B	2.82 ± 0.08	2a ₁	2.69 (0.85)	3a ₁	2.52 (0.85)
C	3.09 ± 0.04	1b ₂	2.97 (0.85)	2b ₂	3.01 (0.85)
			<i>NaAl₄⁻</i>		
X	2.04 ± 0.05	3a ₁	1.92 (0.86)	1b ₁	1.83 (0.85)
A	2.09 ± 0.05	1b ₁	2.05 (0.85)	4a ₁	1.86 (0.86)
B	2.70 ± 0.05	2a ₁	2.52 (0.86)	3a ₁	2.31 (0.85)
C	2.96 ± 0.05	1b ₂	2.86 (0.84)	2b ₂	2.83 (0.84)
			<i>CuAl₄⁻</i>		
X	2.32 ± 0.06	2b ₁	2.32 (0.86)	2b ₁	2.18 (0.86)
A	2.35 ± 0.06	4a ₁	2.39 (0.87)	6a ₁	2.21 (0.86)
B	3.24 ± 0.09	2b ₂	3.35 (0.85)	5a ₁	3.24 (0.85)
C	3.84 ± 0.06	3a ₁	3.65 (0.86)	3b ₂	3.33 (0.86)

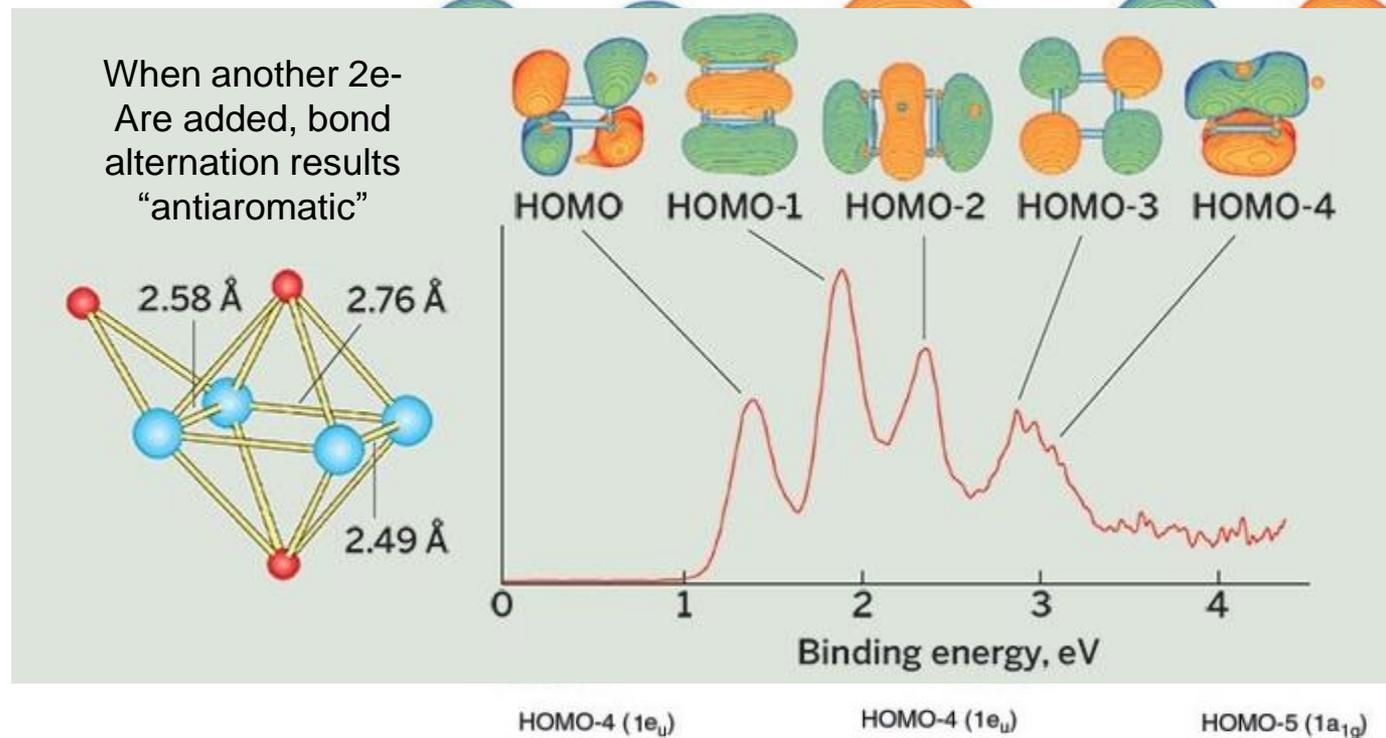


Based on theory, the square pyramid structures are more correct

Lack of bond alteration in these structures

Square Planar Aluminum Clusters

Aromaticity

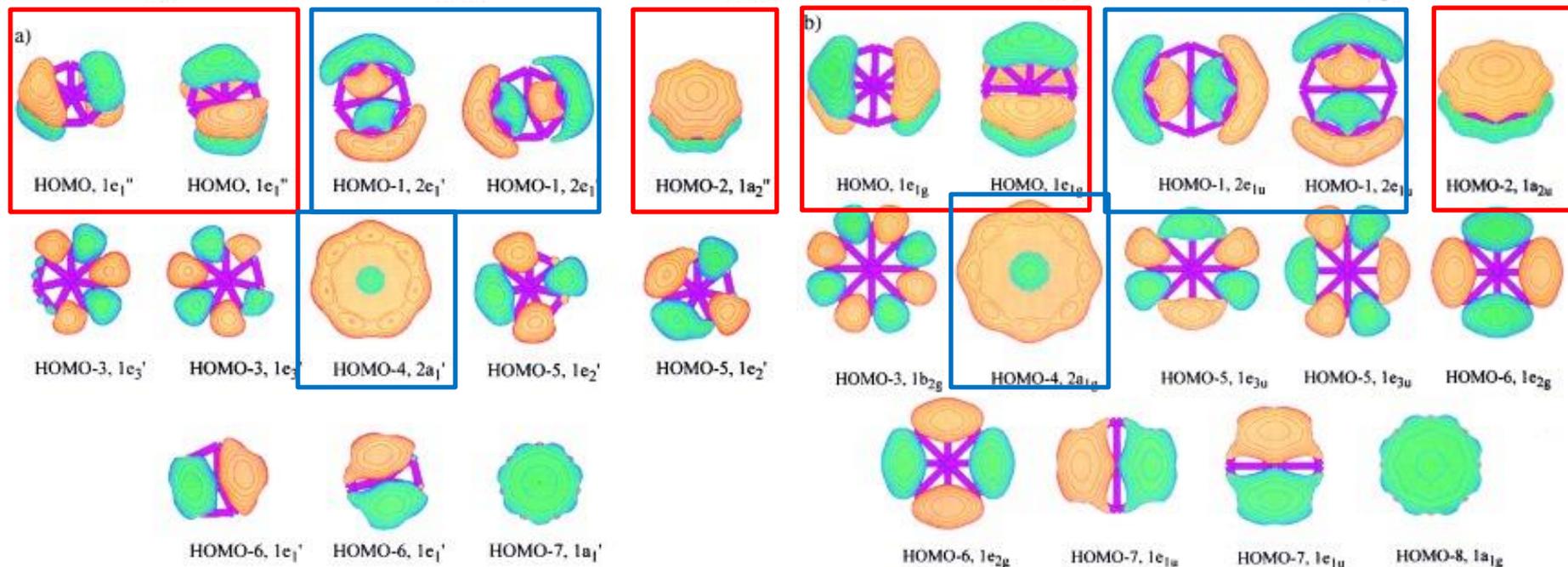
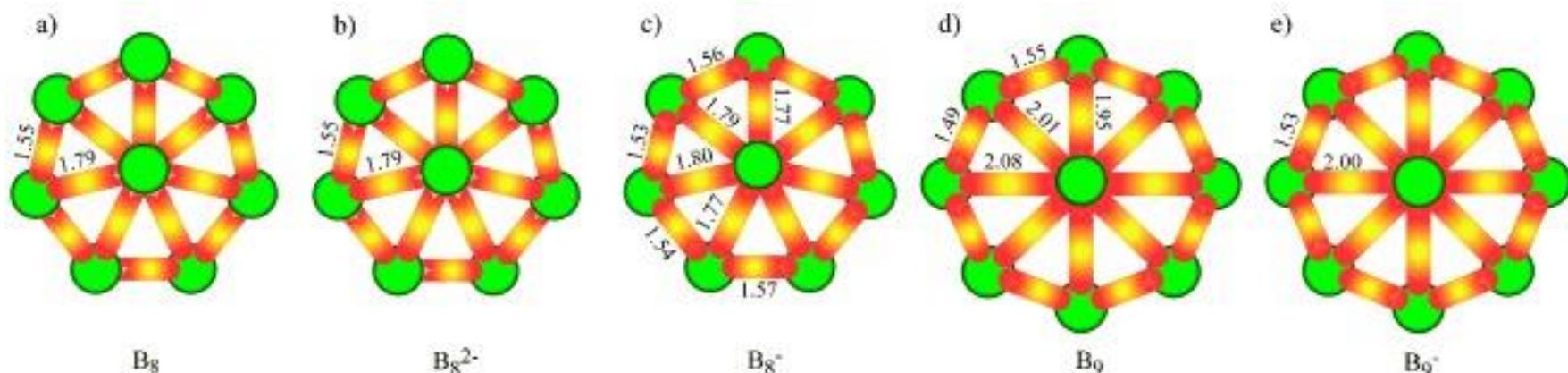


HOMO is doubly occupied delocalized π -orbital

Based on calculated MOs, planar structure, and tendency to form (relative stability), Boldyrev and Wang consider Al_4^{2-} aromatic.

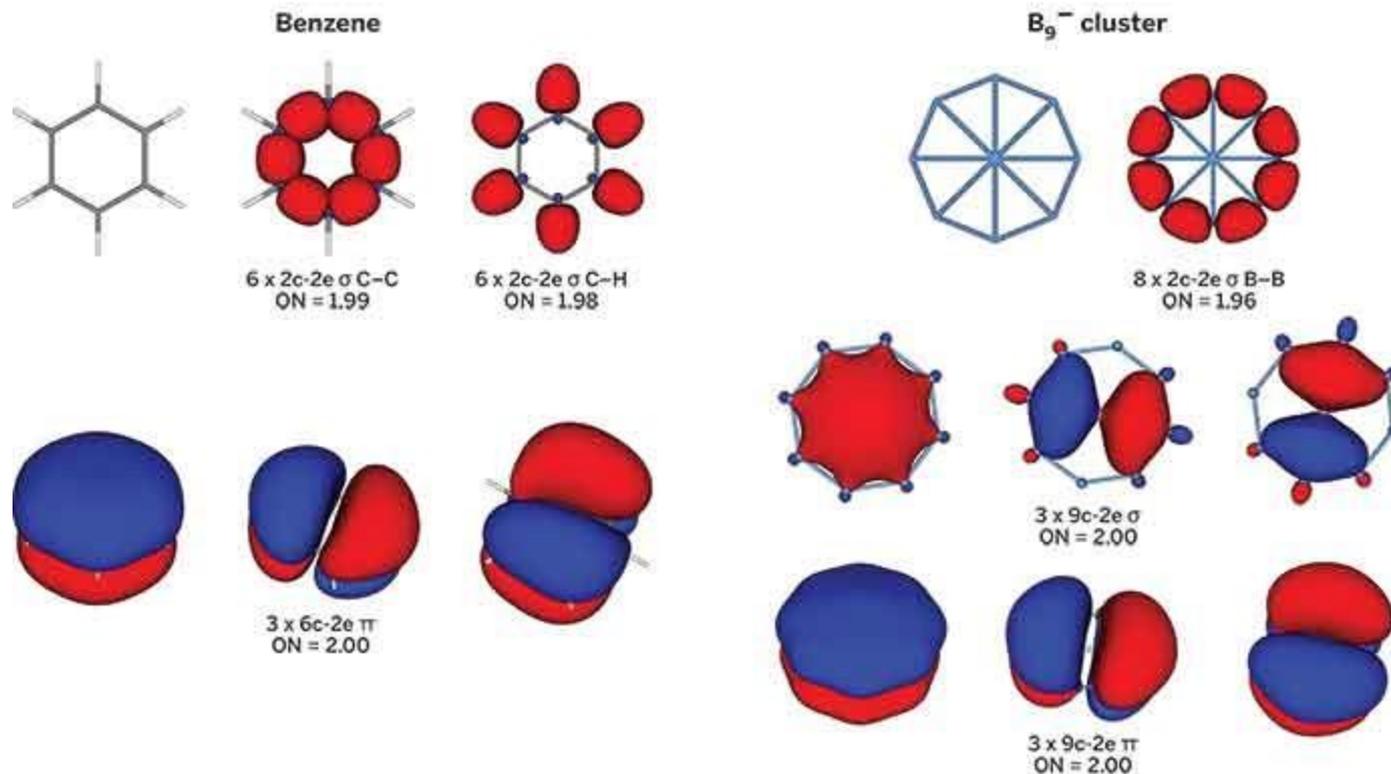
Boron Wheels

“double aromaticity”



Boron Wheels

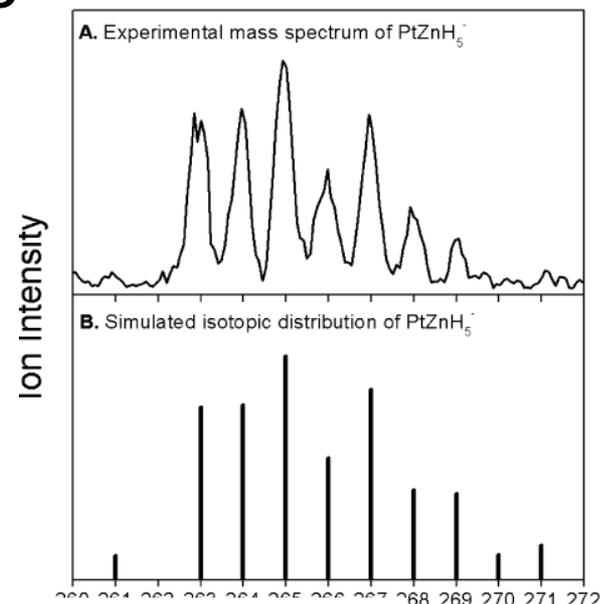
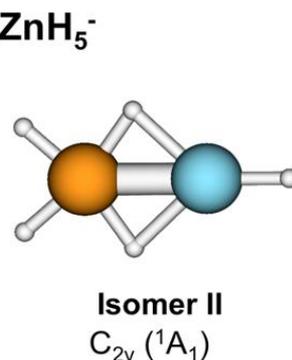
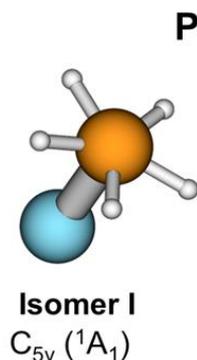
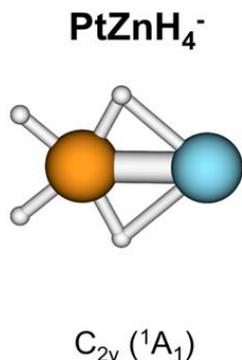
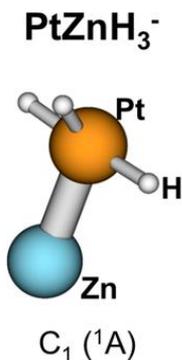
Comparison of B_9^- and Benzene



Claim both π - and σ -aromaticity

- Planar, cyclic system
 - Obeys $4n+2$ rule in π - and σ -aromatic systems
 - “Relatively” stable compared to other B_8 and B_9 species
- Aromatic?

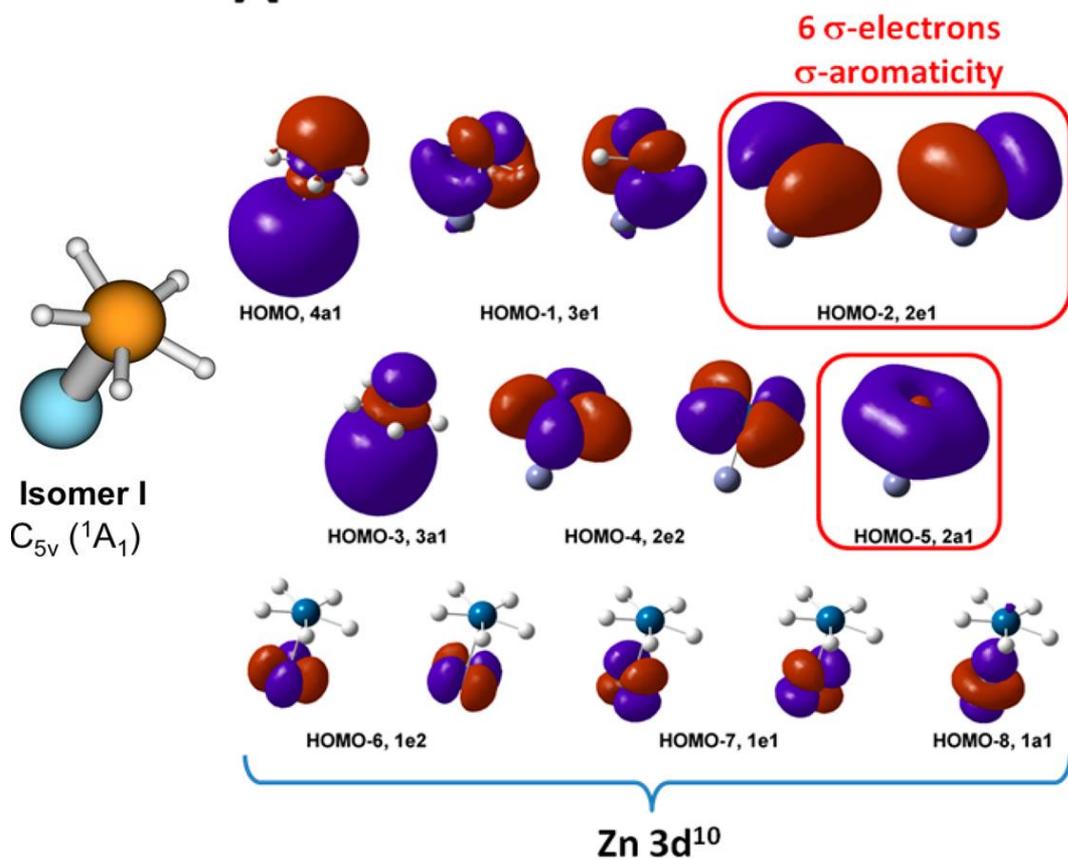
Platinum Hydrides σ -aromaticity



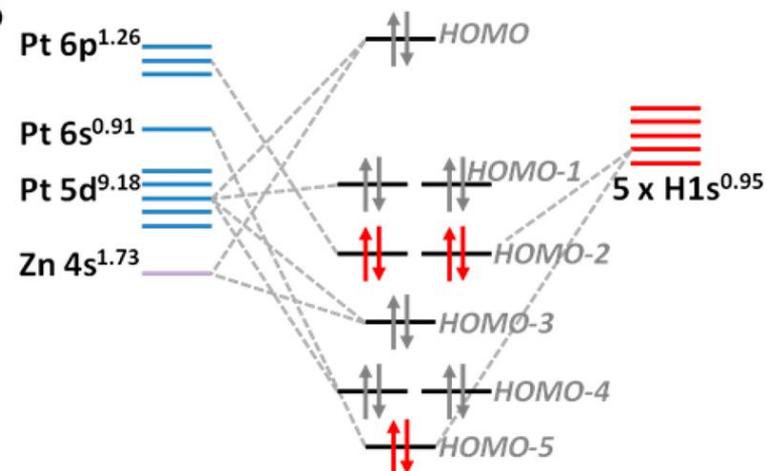
peak	expl. VDE/EA	MO	TD-UPBEPBE, ^a VDE/ADE	TD-UPBEPBE, ^b VDE/ADE	CCSD(T))
Isomer I					
X	2.75/2.5	HOMO	2.71/2.58	2.70/2.51	2.50 ^c
		HOMO-1	4.48 ^d	4.50 ^d	
		HOMO-2	4.93 ^d	4.92 ^d	
		HOMO-3	5.83	5.91	
		HOMO-4	7.12 ^d	7.13 ^d	
Isomer II					
X	2.75/2.5	HOMO	3.68	3.65	3.84 ^c
		HOMO-1	3.97	4.02	
		HOMO-2	4.17	4.19	
		HOMO-3	4.46	4.67	
		HOMO-4	4.70	5.17	

ZnPtH₅⁻

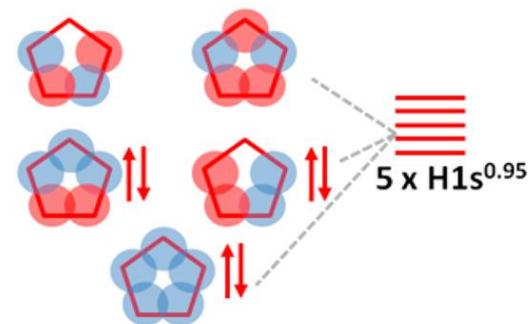
A



B



C



What does aromaticity really mean in a chemical context?

- The presented examples highlight the nebulous nature of the concept of aromaticity
- Is aromaticity just a fancy word for extreme electron delocalization?
- Does σ -electron delocalization in a system count as aromaticity?
- Must something be fully isolable to be considered aromatic?
 - R. Hoffmann places a “kinetic persistence” requirement on aromaticity

Conclusions

- Aromaticity is a rather nebulous concept
- Is defined as a “relative” stabilization
 - Requires a frame of reference
- Assigning aromatic stabilization to stabilized high energy species may go against the original spirit of the classical concept of aromaticity
- The simple physical organic test question of “is this aromatic?” is an ideal case
 - Is aromaticity a term that should be replaced?



Relevant Reviews

- Chem Rev 2005, vol. 105. Entirely about different types of aromaticity

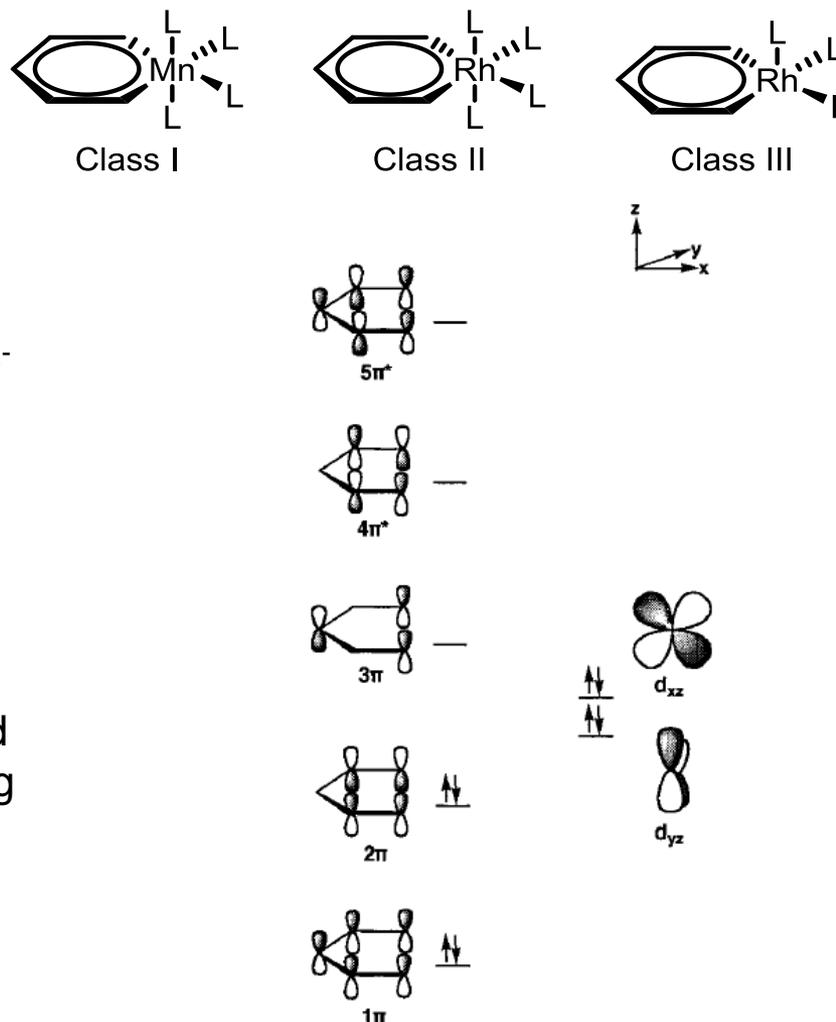


Metallobenzenes

- Transition metal containing
- Main group containing
- Alkali and Alkaline earth metal containing

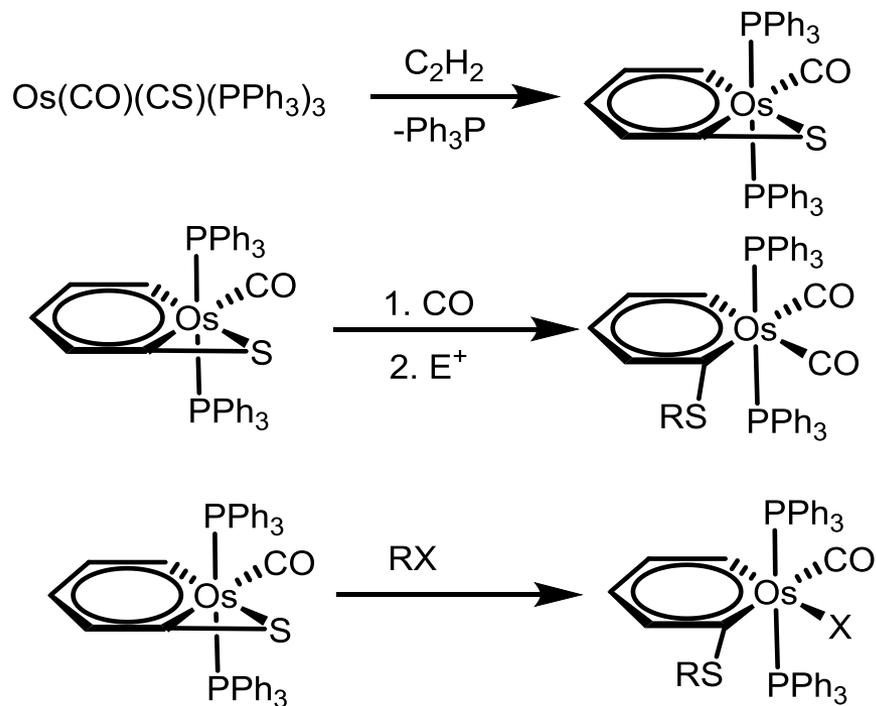
Theory – Thorn and Hoffmann

- Attempted to figure out why 5 member metallocycles do not exhibit π -delocalization
- Predicted 3 classes (L is a neutral 2e-donor ligand)
- Treated the carbon fragment as a monoanionic ligand $C_5H_5^-$, donating 4e⁻ to the metal center
- Thorn/Hoffmann believed the two remaining pi electronics come from the d_{xz} orbital of the metal interacting with the 3 π anion orbital
 - Backbonding
- Schleyer proposes that both the d_{xz} and d_{yz} orbitals are involved, with d_{yz} mixing with 2 π to generate a new 2 π bonding MO and a lower energy 4 π^* MO



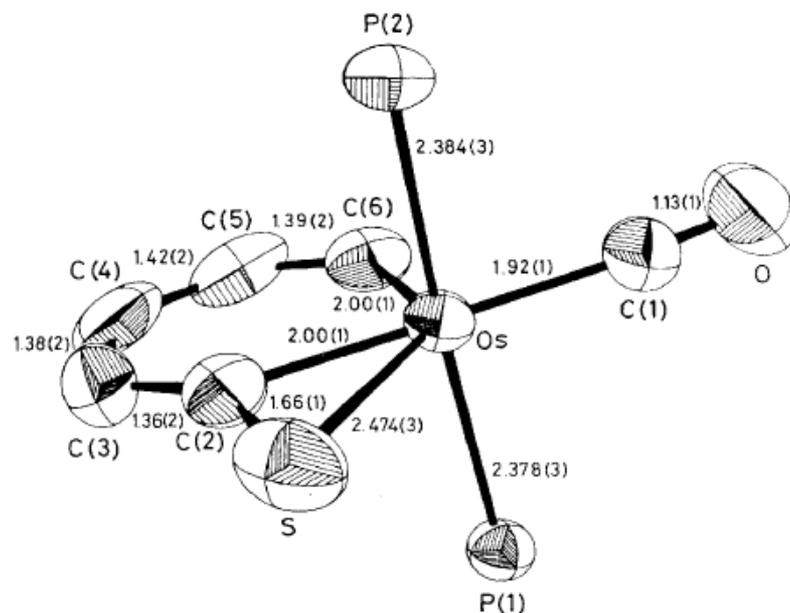
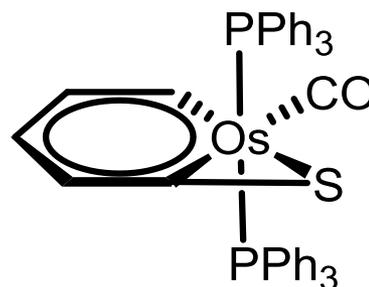
Osmabenzene

The first example of a metallobenzene



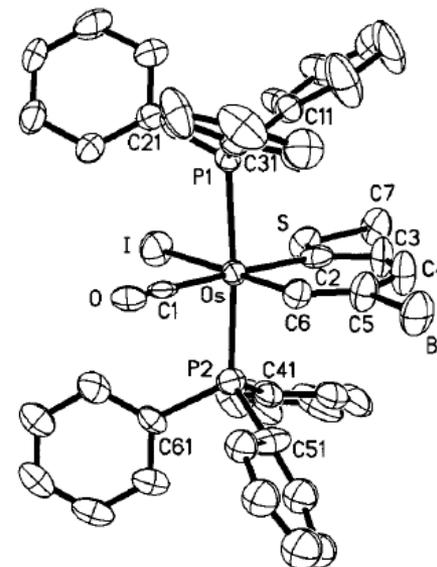
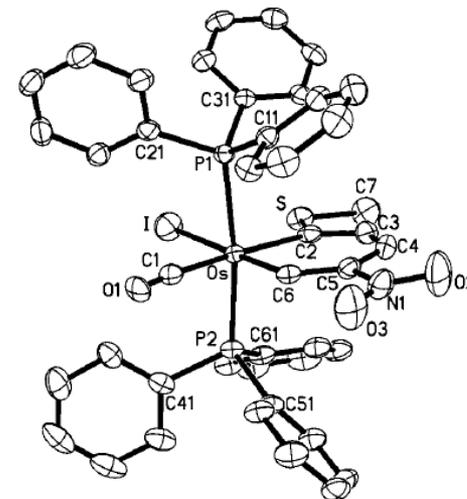
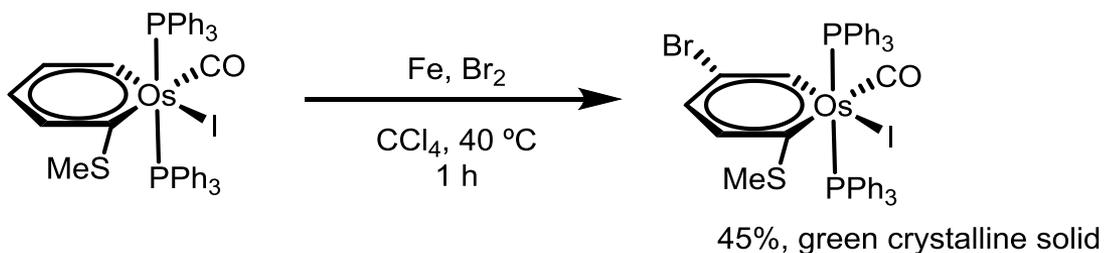
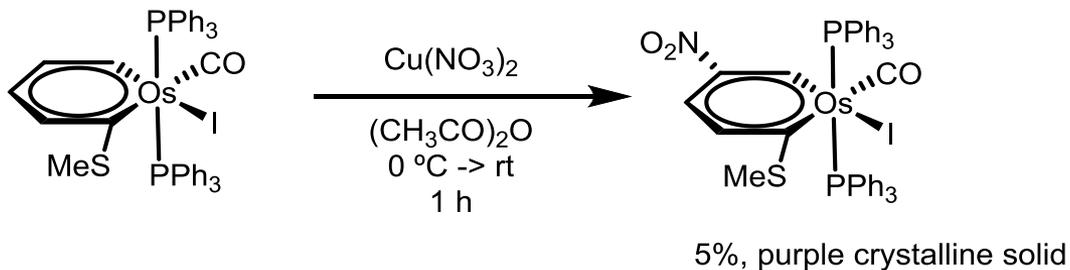
Is Osmabenzene aromatic?

- C2-C5 C-C bond lengths nearly identical
- C-Os bonds intermediate between single and double bonds
- NMR: C3-5 ^1H has 3 overlapping signals at $\delta 7.28$
 - Due to ring current anisotropy
 - C2/C6: $\delta 13.95$ due to effect of Os

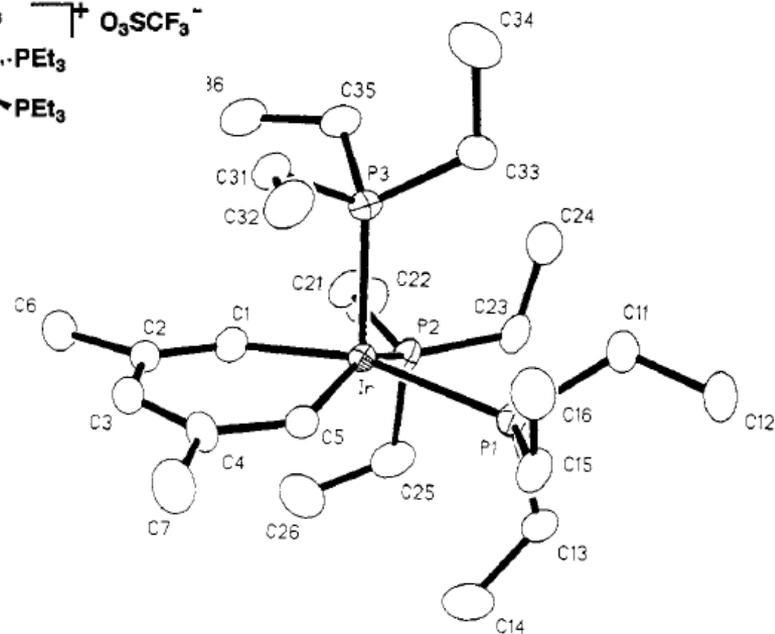
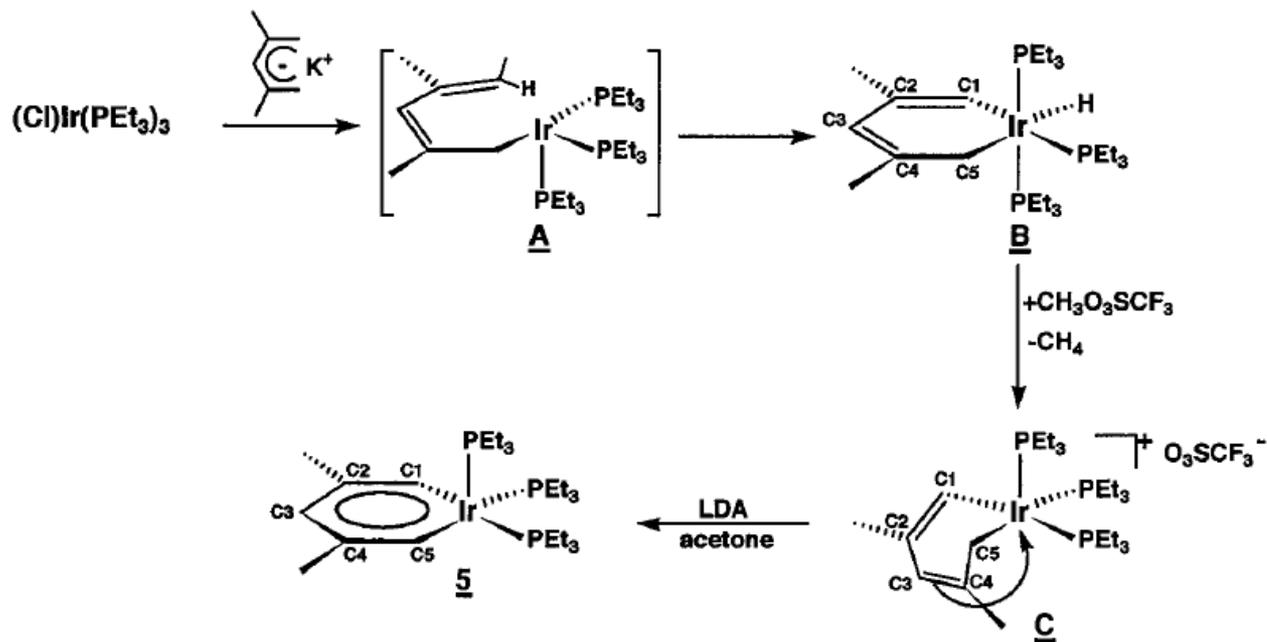


Reactions of Osmabenzene

- Osmabenzenes undergo electrophilic aromatic substitution

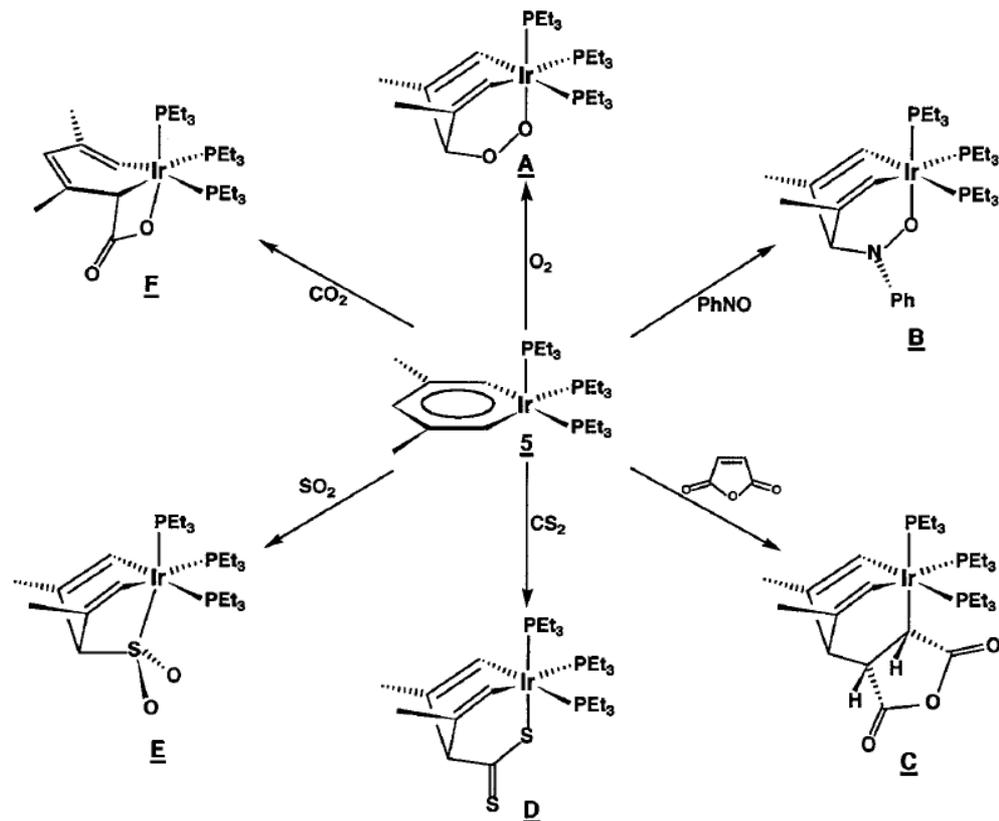


Iridium Metallobenzenes



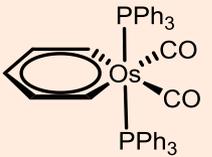
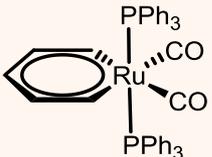
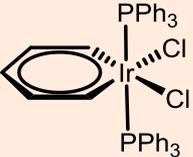
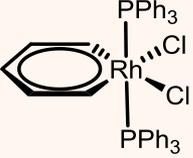
In the case of iridiumbenzenes, the iridium is displaced significantly out of the plane of the ring.

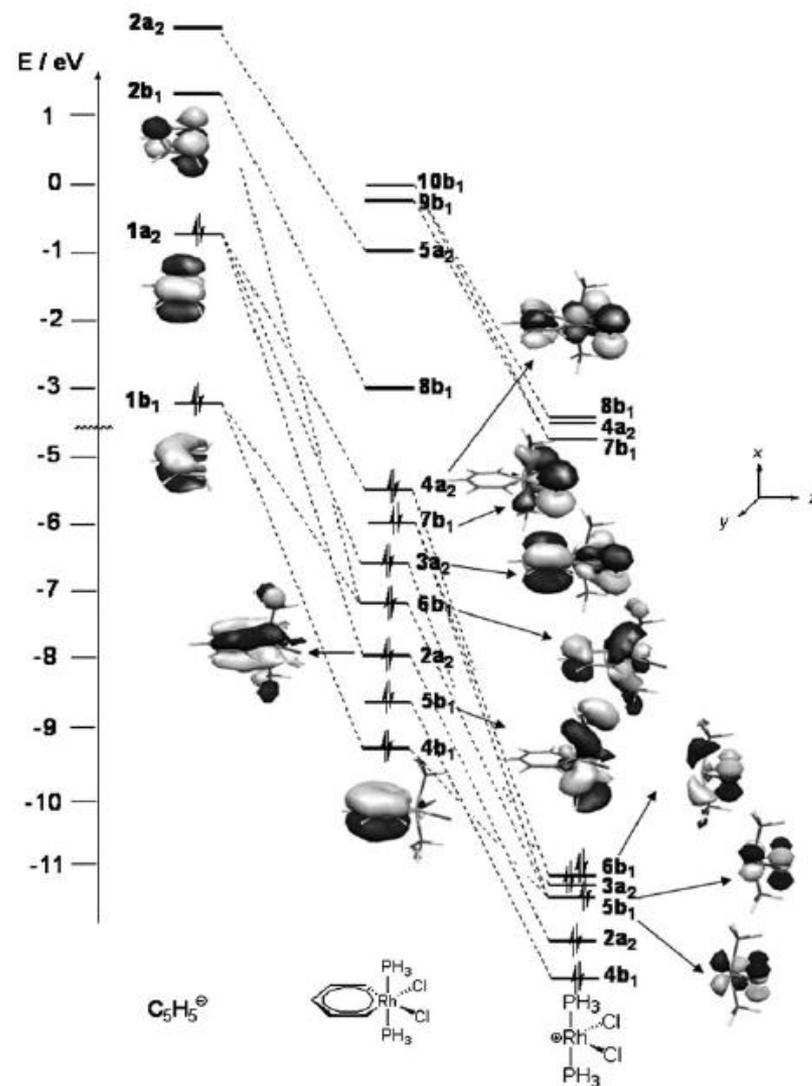
Reactions of Iridium benzenes



The reactions observed seem to indicate that iridium-metallobenzenes are not as aromatic as osmabenzenes. However, one must take into account the difference in the metal center.

Metallobenzenes as 10π Huckel systems

Metallobenzene	ASE (kcal/mol)
	17.6
	17.7
	33.5
	33.4
	37.6



Metallobenzene Summary

- Isolable compounds
- Computational studies indicate that these compounds possess aromatic stabilization that can approach that of benzene
- Exhibit negligible C-C bond alternation
- Have NMR characteristics that show evidence of a π -ring current
- Depending on the metal center, exhibit chemical reactivity similar to benzene
- Aromatic?