



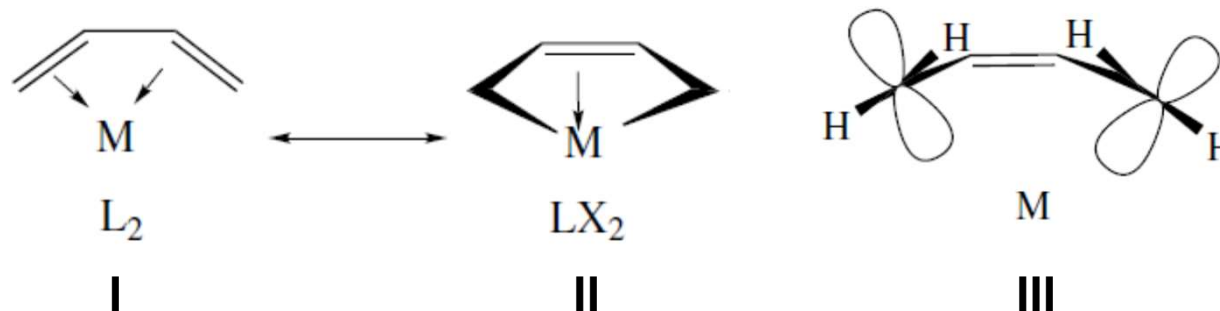
University of Lucknow | Centenary Year
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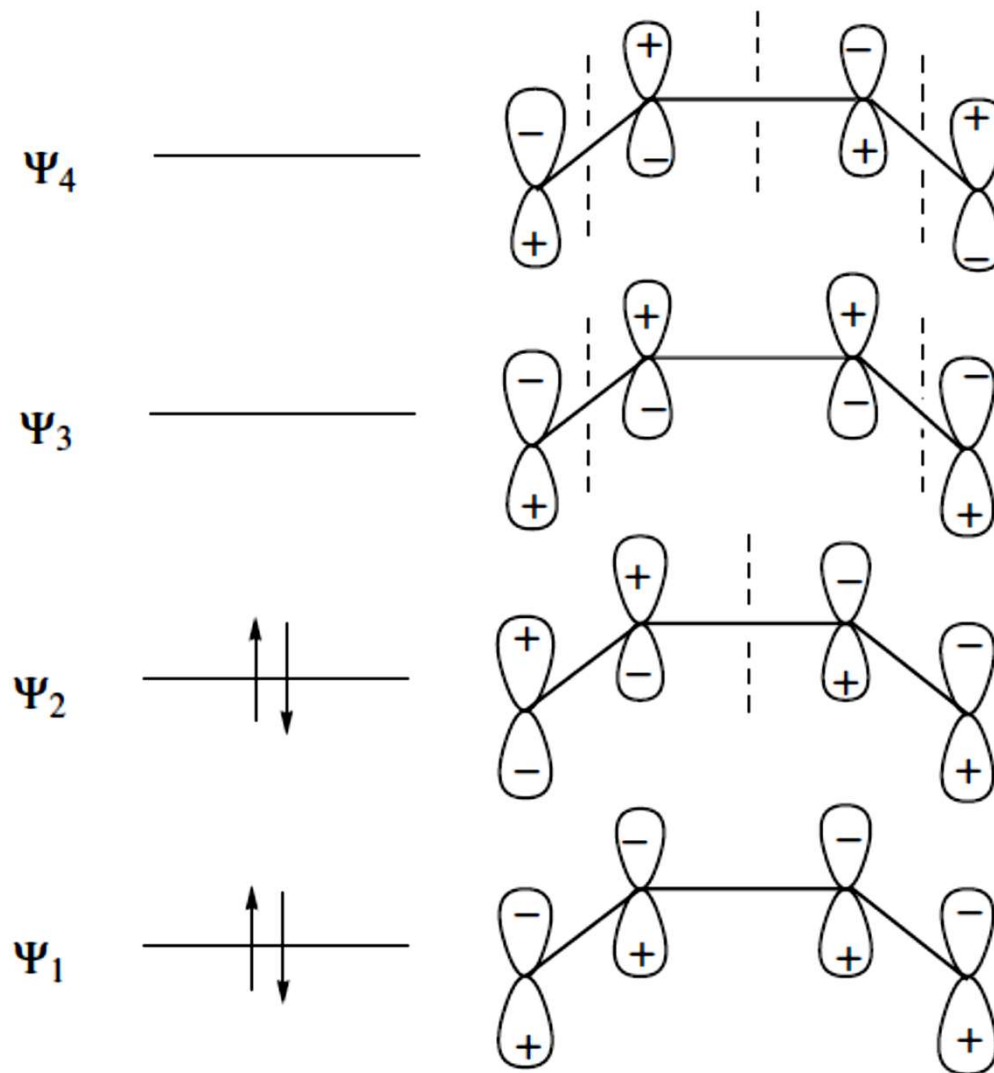
Transition Metal Dienes: Bonding, Syntheses and Reactions

Bonding and Electronic Features

- This ligand usually behaves like a 4e donor in its *cisoid* conformation (I). This L_2 (diene or π_2) form is analogous to the Chatt–Dewar extreme for alkenes, while the LX_2 (enediyl or $\sigma_2\pi$) form (II) is related to the metalacyclopropane extreme.



- The first is rarely seen in pure form but (butadiene)Fe(CO)₃ possesses an intermediate character, with the C1C2, C2C3, and C3C4 distances about equal (1.46 Å) and C1 and C4 further from the metal than C2 and C3.
- Form II becomes more important with increase in the back donation.
- Bound to the strongly back-donating Hf(PMe₃)₂Cl₂ a d² system, 1,2-dimethylbutadiene shows an extreme LX₂ (II) bonding pattern.
- The substituents at C1 and C4 twist approximately 20°–30° out of the plane of the ligand and bend back strongly so that the corresponding p orbitals can overlap better with the metal (III).
- The C1C2, and C3C4 distances [1.46 Å (average)] are much longer than C2C3 (1.40 Å) and C1 and C4 are closer to the metal than C2 and C3 by 0.18 Å.

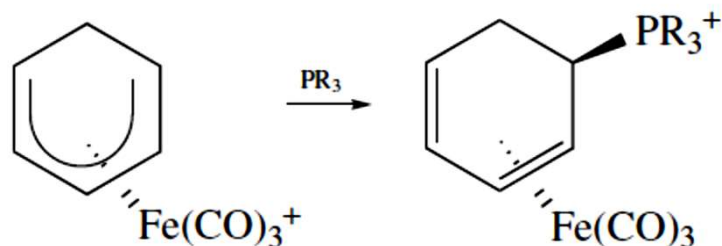
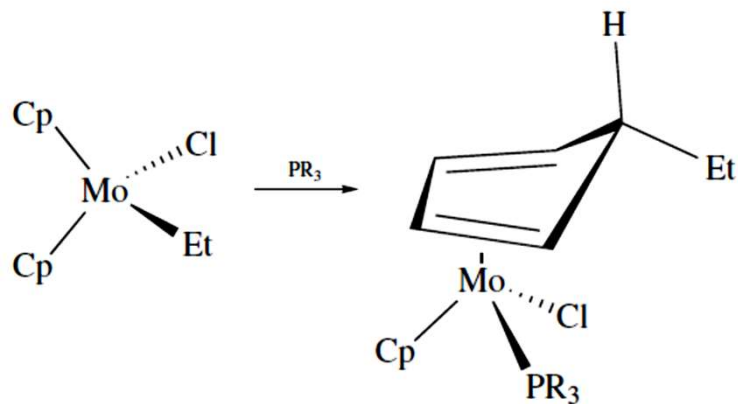
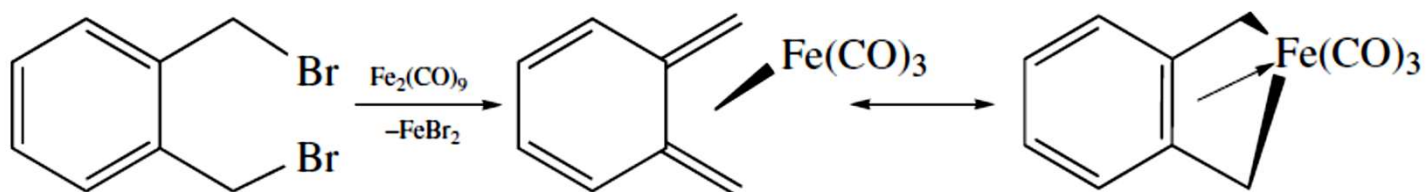


Electronic structure of butadiene. An electron-rich metal will tend to populate Ψ_3 ; an electron-poor metal will tend to depopulate Ψ_2 .

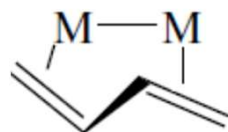
- The frontier orbitals of the butadiene, ψ_2 (HOMO) and ψ_3 (LUMO) are expected to be the most important in bonding to the metal.
- The molecular orbital diagram (in the previous slide) shows that both the depletion of electron density in ψ_2 by σ donation to the metal and population of ψ_3 by back donation from the metal lengthens C1C2 and shortens C2C3 because ψ_2 is C1C2 antibonding and ψ_3 is C2C3 bonding.
- Protonation always takes place at C1 because the HOMO, ψ_2 , has its highest coefficient there.
- Therefore, binding to a metal usually depletes the ligand HOMO and fills the ligand LUMO.
- This is the main reason why binding has such a profound effect on the chemical character of a ligand.
- **The structure of the bound form of a ligand is often similar to that of the first excited state of the free ligand because to reach this state we promote an electron from the HOMO to the LUMO, thus partially depleting the former and filling the latter.**

Syntheses

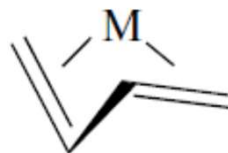
- Butadiene complexes are usually prepared in ways very similar to those used for alkenes, but some methods specific to diene complexes are presented below:



- The binding of butadiene in the transoid form is much rarer.
- But such bonding is found in $\text{Os}_3(\text{CO})_{10}(\text{C}_4\text{H}_6)$ in which the diene is η^2 bound to two different Os centers.

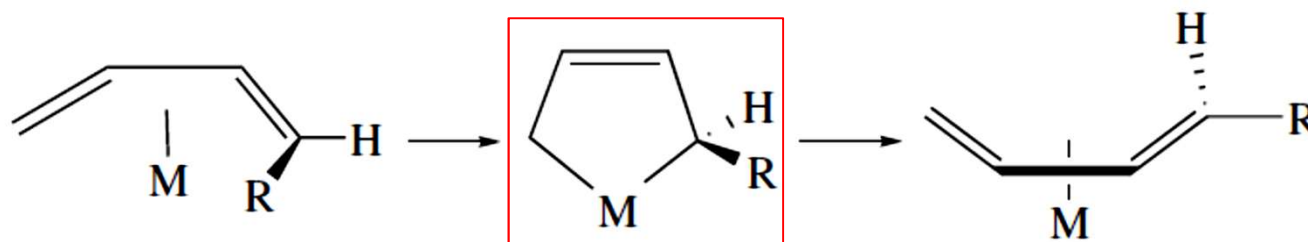


- In $\text{Cp}_2\text{Zr}(\text{C}_4\text{H}_6)$, the diene is bound to a single Zr.



- In the case of $\text{Cp}_2\text{Zr}(\text{C}_4\text{H}_6)$, the cisoid isomer too exists, but it rearranges to give a 1 : 1 thermodynamic mixture of the two forms on standing; photolysis leads to the trans form.

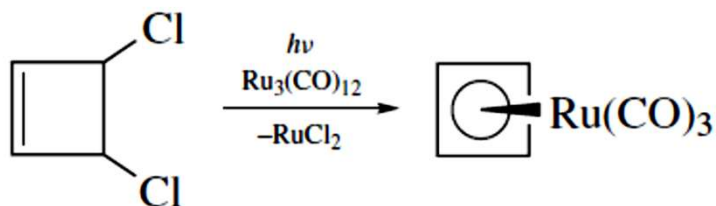
- The “envelope shift” is also sometimes observed. It exchanges the anti and syn substituents on the diene via an X_2 -type metalacyclic intermediate, in which the central C=C group must be uncomplexed (**the highlighted central structure**) because the metal lies in the plane of this C=C group and orthogonal to the C=C π electrons.



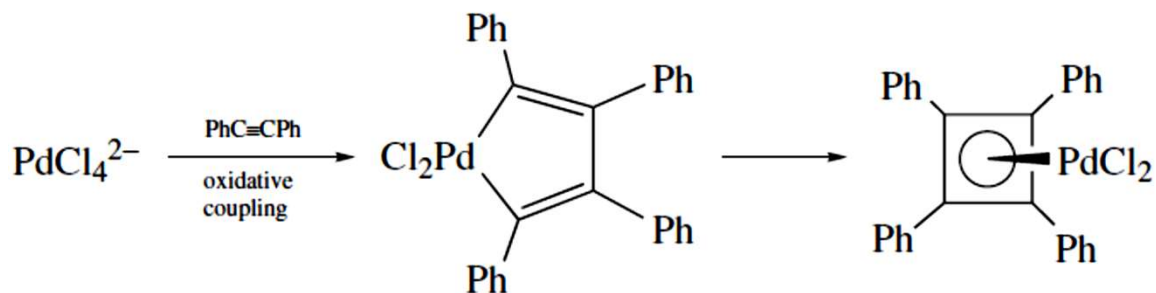
Cyclobutadiene complexes

- With cyclobutadiene, the complexes are very stable and have been known for many years.
- But the free dienes are so highly reactive that stable examples were reported only much later.
- The free molecule, with four π electrons, is antiaromatic and rectangular, but the ligand is square and seems to be aromatic.
- The metal must stabilize the diene by populating the LUMO of the free diene by back donation; by gaining partial control of two more π electrons, this gives the diene an electronic structure resembling that of the aromatic six π -electron dianion $R_4C_4^{2-}$;
- Also, ligand-to-metal σ donation prevents the ligand from accumulating excessive negative charge.
- This is a good example of the free and bound forms of the ligand being substantially different from one another

Synthetic Routes

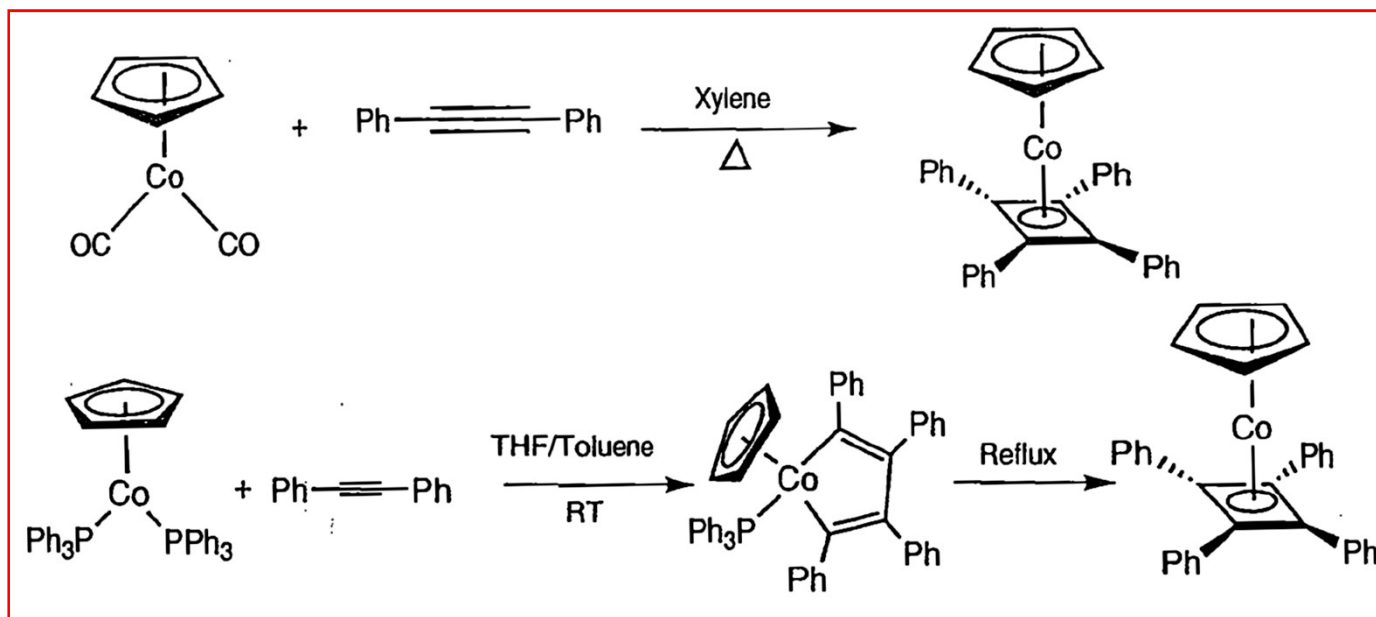
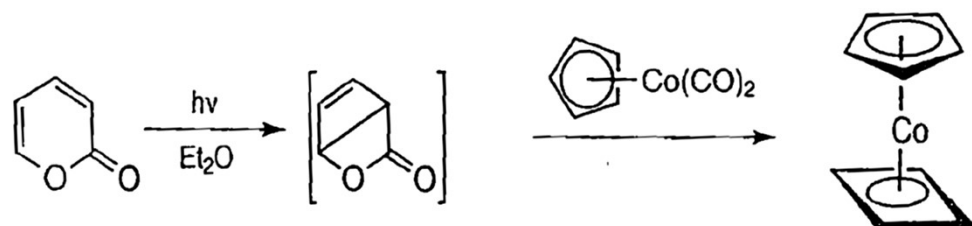
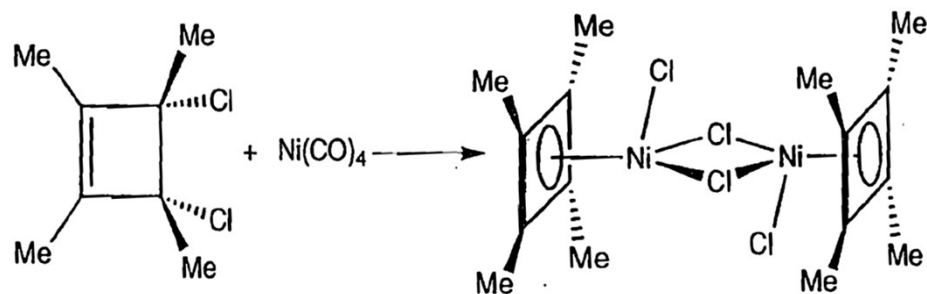


This reaction involves oxidative addition of the dihalide to two $\text{Ru}(\text{CO})_3$ fragments derived from the photolysis of the cluster; then the metals probably disproportionate, so that one becomes the observed product and the other carries away the halides in the form of undefined $\text{Ru}(\text{II})$ halo complexes.

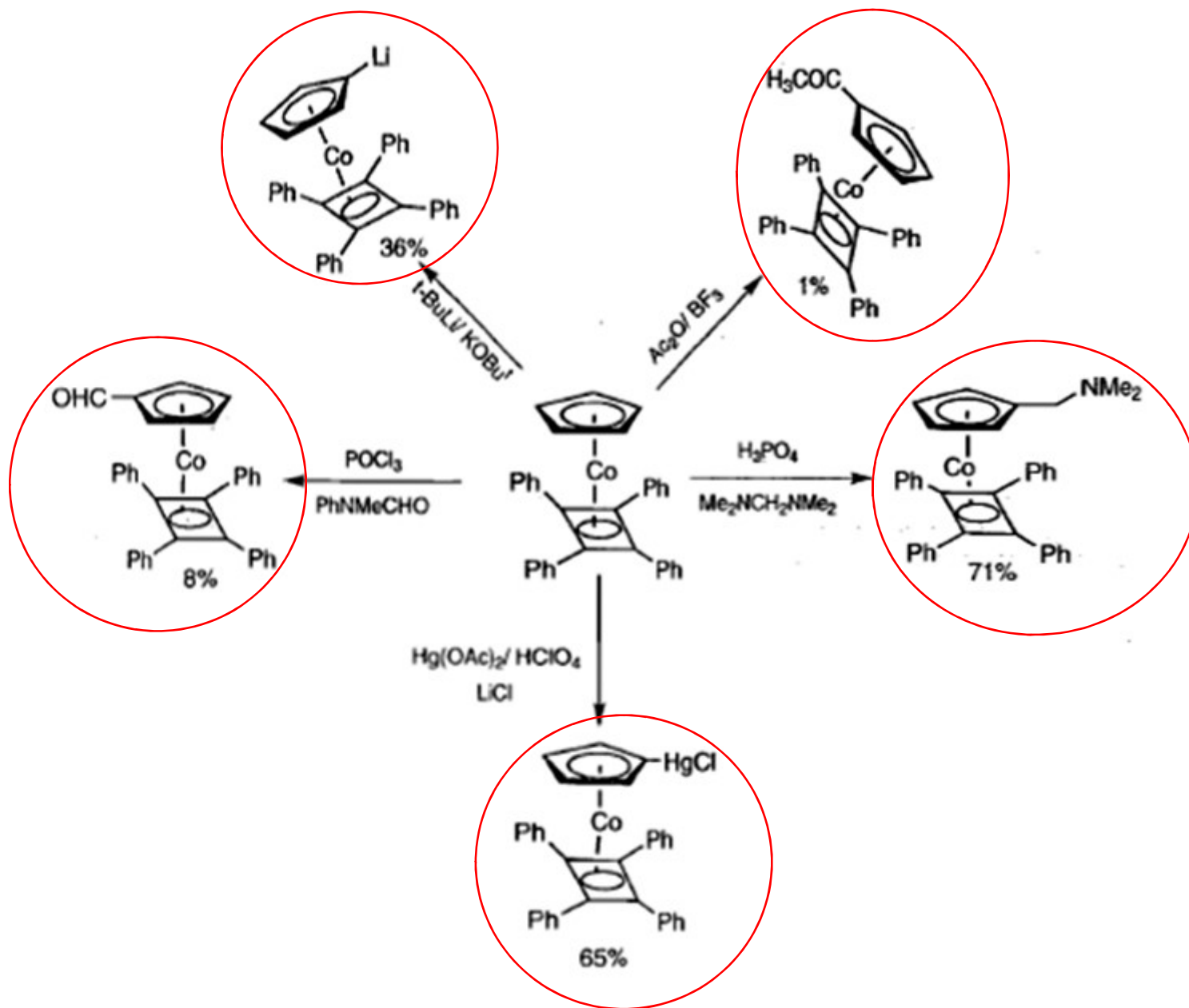


This reaction probably goes by an important general class of reaction, *oxidative coupling*, to give a metalacycle, followed by a reductive elimination of the cyclobutadiene ligand.

Other syntheses



These reactions have already been mentioned in transition metal alkynes



Electrophilic substitution reactions on Cp rings

References

- **Basic Organometallic Chemistry: Concepts, Syntheses and Applications by B. D. Gupta and Anil J. Elias**
- **The Organometallic Chemistry of the Transition Metals by R. H. Crabtree**