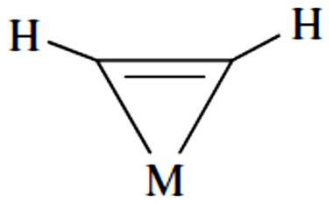
Transition Metal Alkynes: Bonding, Syntheses and Reactions

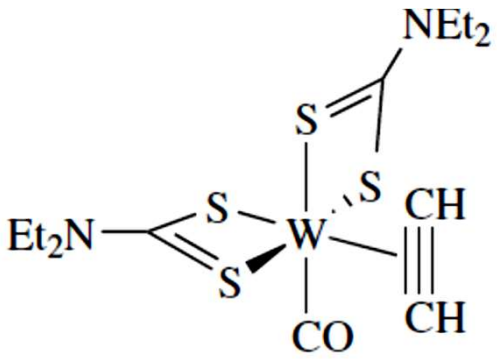
Bonding and Electronic Features

- Alkynes behave in the manner similar to alkenes when they undergo bonding to any transition metal.
- They coordinate far more readily than alkene for stearic (more open, less hindered) and electronic (better donor, $2e^-$ or $4e^-$) reasons.
- But being more electronegative, they tend to encourage back donation and bind more strongly.
- The substituents tend to fold back away from the metal by 30°–40° in the complex, and the M−C distances are slightly shorter than in the corresponding alkene complexes.



- The metalacyclopropene model seems often to be the most appropriate description when alkynes act as $2e^-$ donors.

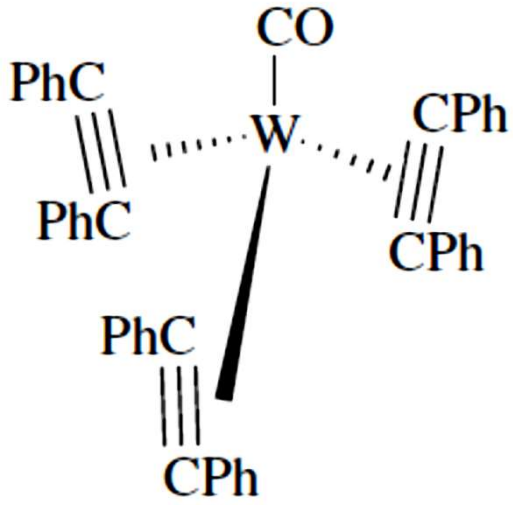
- alkynes can form complexes that appear to be coordinatively unsaturated. For example

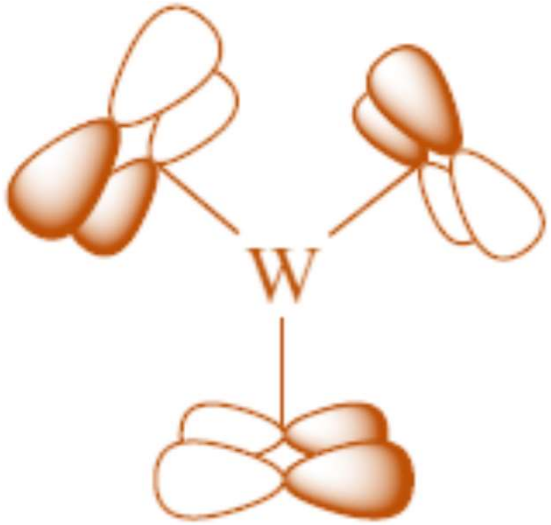


16e- species

if one count the alkyne as a conventional 2e- donor

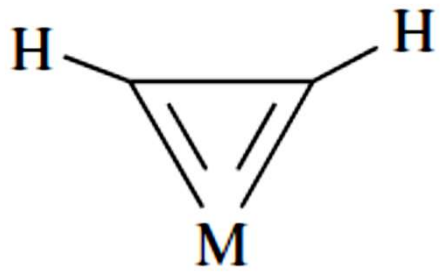
- In such cases the alkyne also donates its second C=C π-bonding orbital, which lies at right angles to the first.
- The alkyne is now a 4e donor and hence the 16e- species can be formulated as an 18e- complex.





- Compound might seem to be a 20e$^-$ complex on the model mentioned in the previous slide, but in fact one combination of ligand π orbitals, finds no match among the d orbitals of the metal, and so the true electron count is 18e$^-$.

- An extreme valence bond formulation of the $4e^-$ donor form is the bis-carbene.

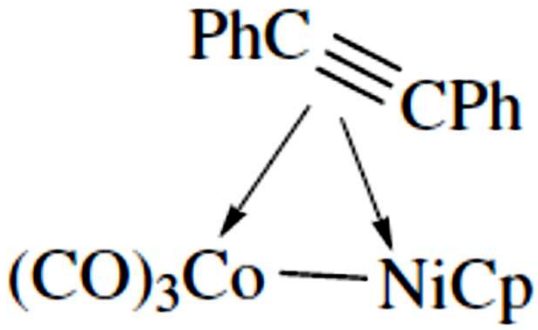


- Four electron alkyne complexes are rare for d^6 metals because of a $4e^-$ repulsion between the filled metal dπ and the second alkyne C=C π-bonding pair.

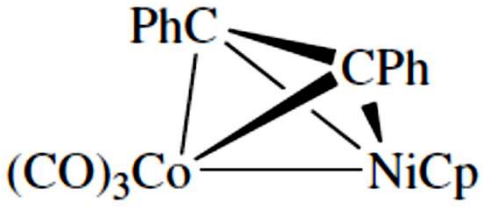
- When the free alkyne has a structure that leads to bending of the C≡C triple bond, this induces strain, which is partially relieved on binding.
- Cyclohexyne and benzyne are both highly unstable species that bind very strongly to metals, as in $[(Ph_3P)_2Pt(\eta^2\text{-cyclohexyne})]$.

$$Cp^*TaMe_3Ph \rightarrow Cp^*TaMe_2(\eta^2\text{-benzyne}) + MeH$$

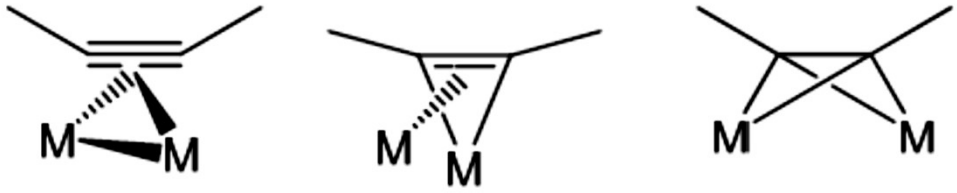
- Alkynes readily bridge an M−M bond, in which case they can behave as conventional $2e^-$ donors to each metal.



- The alternative tetrahedrane form is the equivalent of the metalacyclopropane picture for such a system.

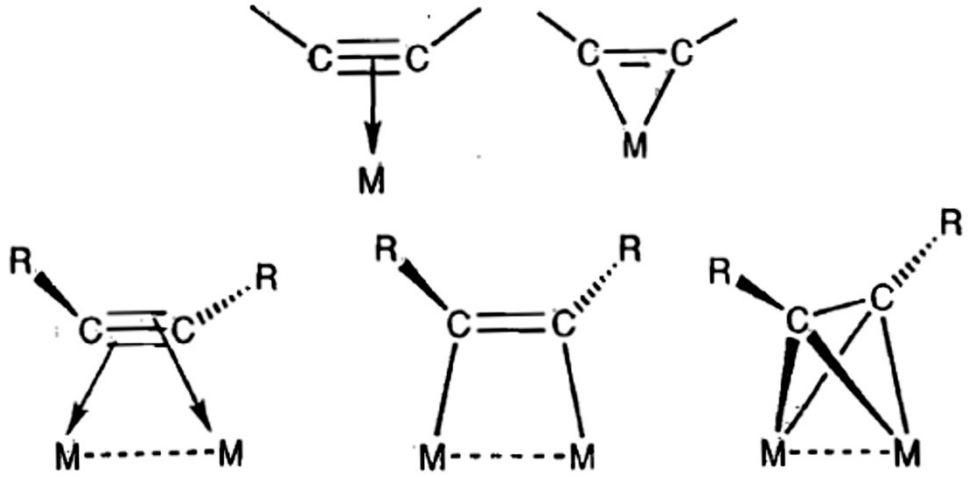


- The bridging metal alkyne complexes can be represented as

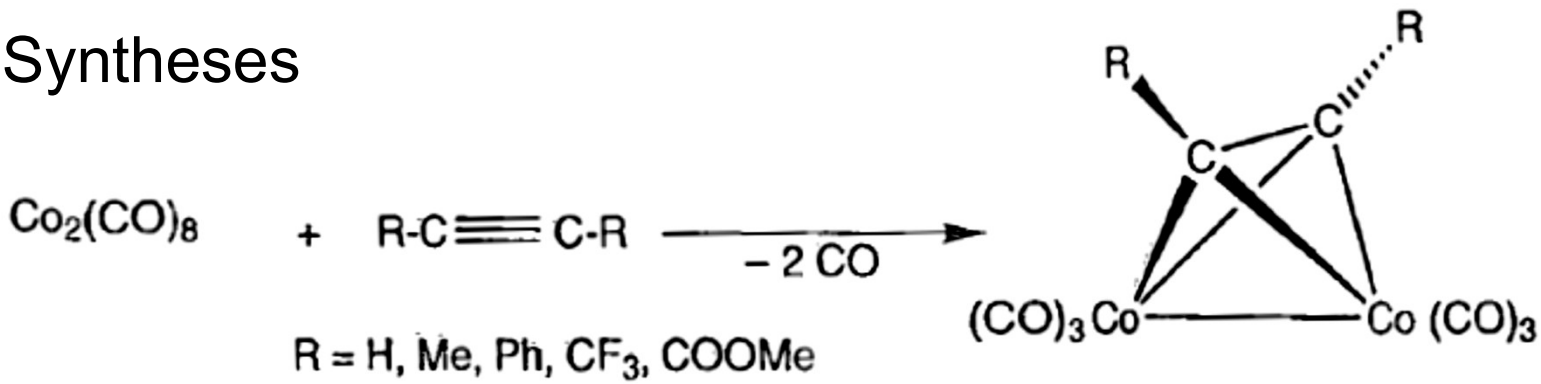


	η^2	η^3	η^4
Ionic model:	**4e (0)**	**6e (2-)**	**8e (4-)**
Covalent model:	**4e (0)**	**4e (0)**	**4e (0)**

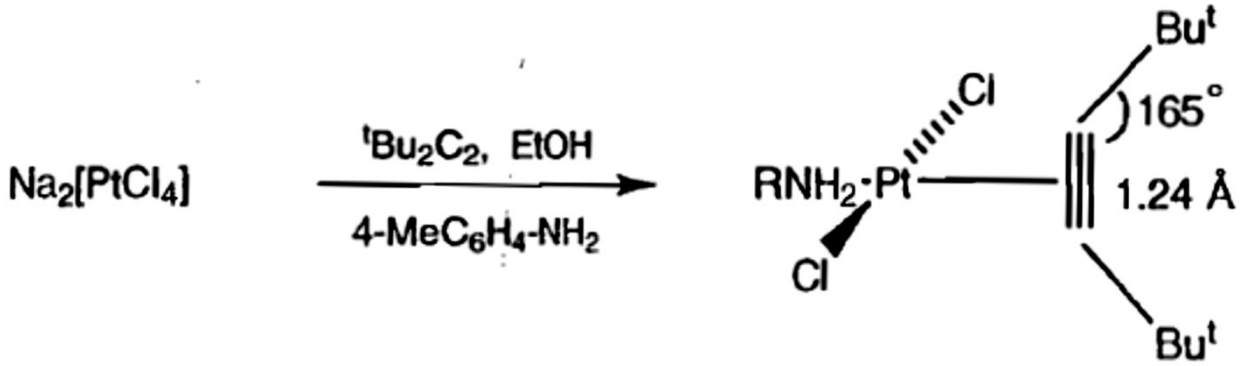
- Like alkenes, the bonding of alkynes to metal centers too exhibit different orientations w.r.t. plane of the metal complex.
- For example, in Pt(II) complex $PtCl_2(ArNH_2)(Bu^t)C{\equiv}C(Bu^t)$, the orientation of the alkyne is perpendicular to the square plane of the molecule whereas in Pt(0) complex $Pt(PPh_3)_2(PhC{\equiv}CPh)$ there is in plane bonding of the diphenyl acetylene w.r.t. the square plane of the molecule.
- In totality all the possible bonding modes of alkynes with transition metals can be represented as



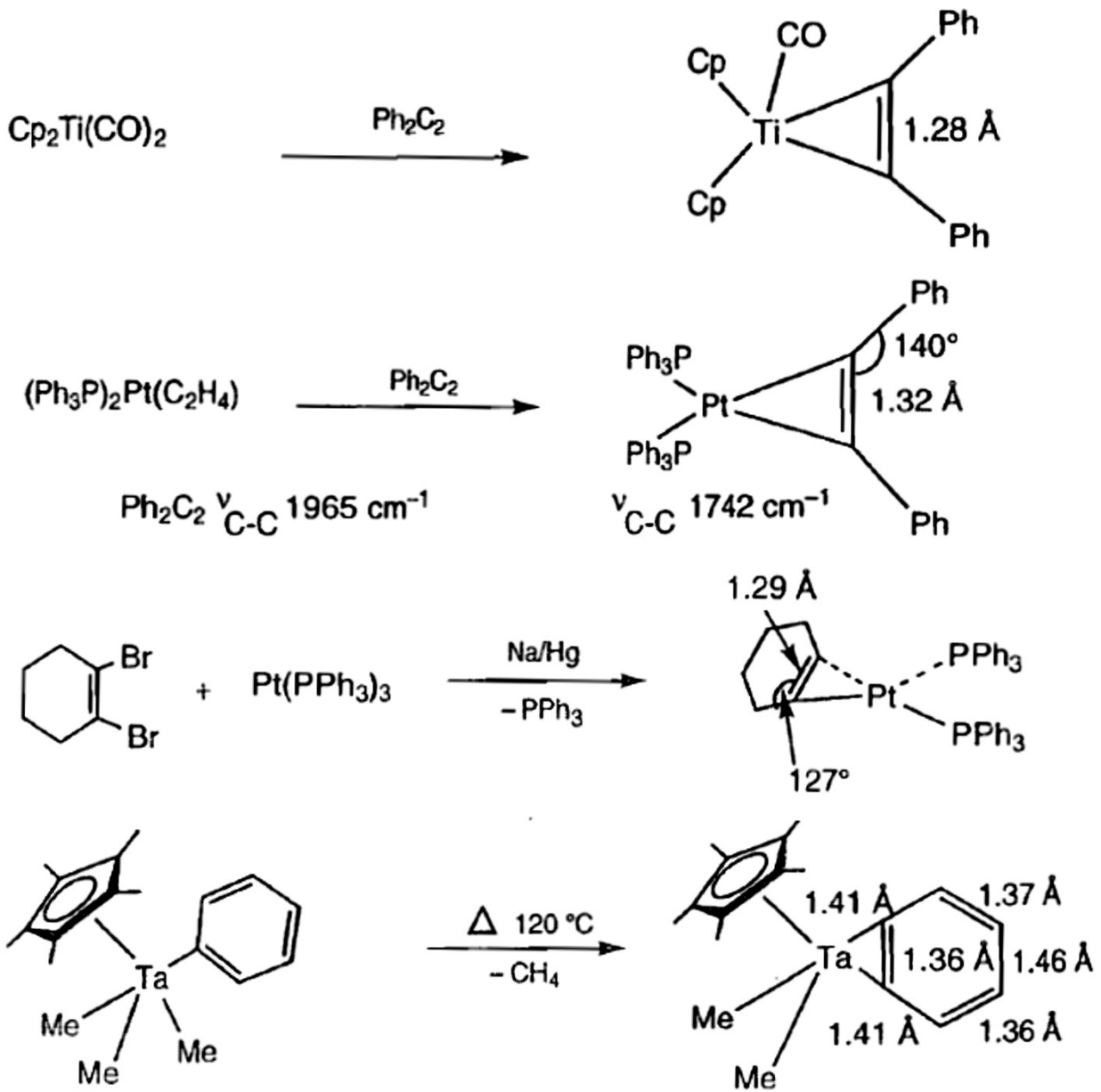
Syntheses



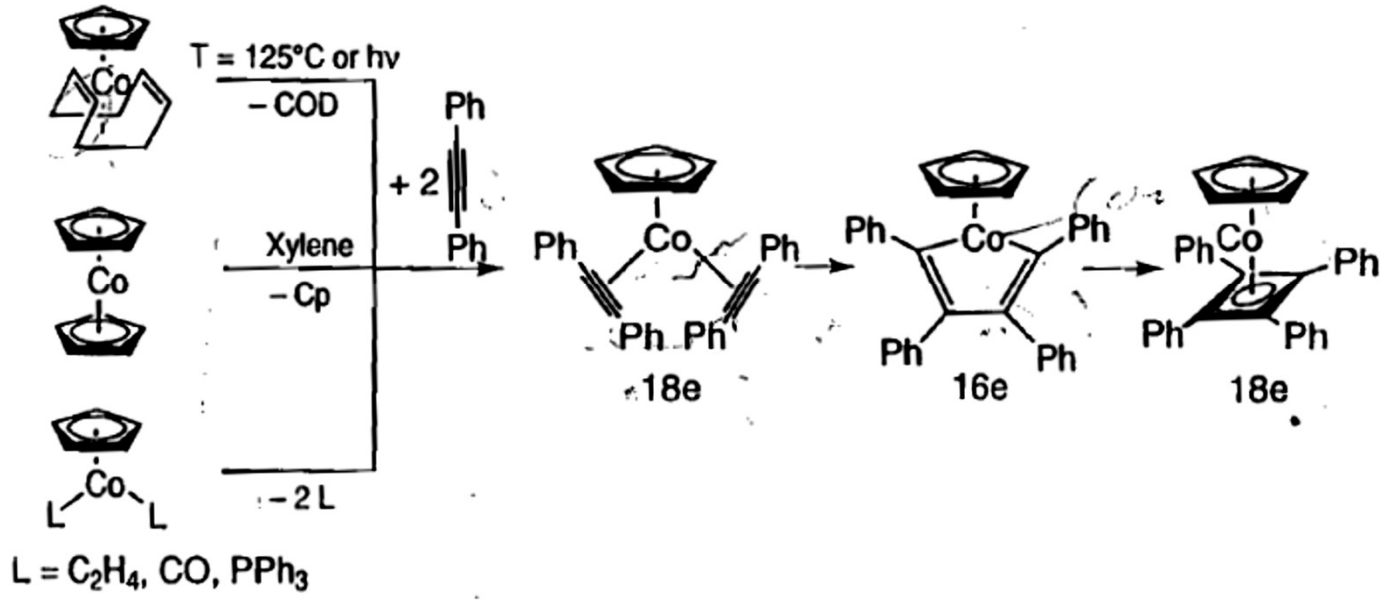
Coordination to the metal center lead to weakening in C≡C bond strength which is evident from IR spectroscopy



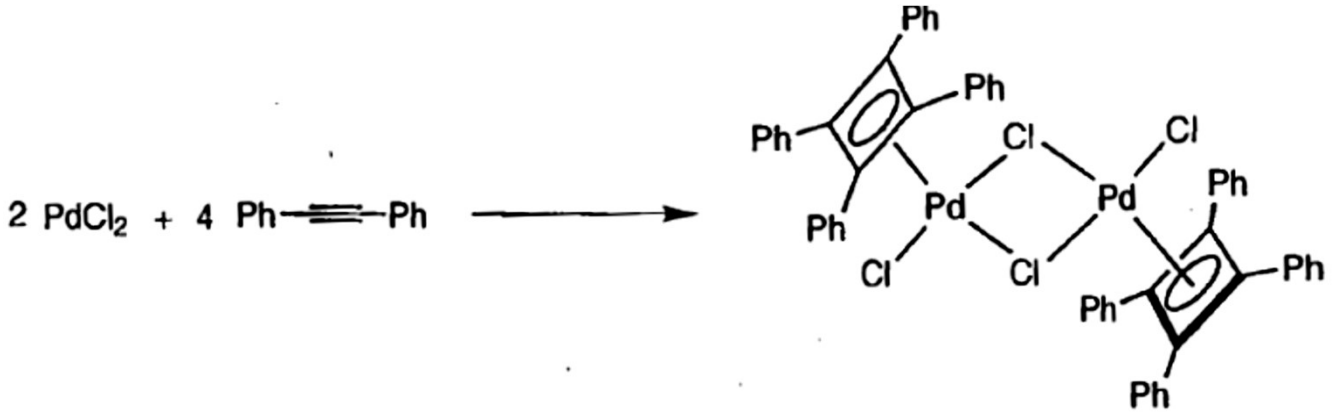
the orientation of the alkyne is perpendicular to the square plane of the molecule and Bu^t group folds away back too.

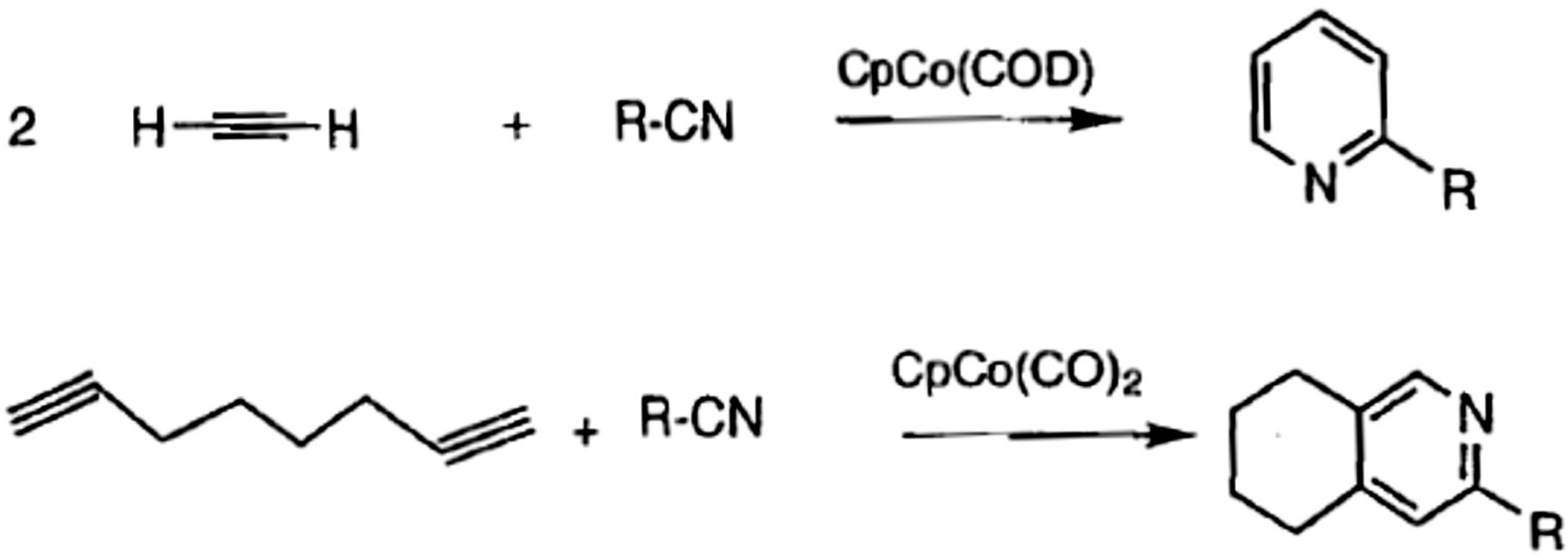

Cp2Ti(CO)2
Ph2C2
Cp
CO
Ti
Cp
Ph
1.28 Å
Ph
(Ph3P)2Pt(C2H4)
Ph2C2
Ph3P
Pt
Ph3P
Ph
140°
1.32 Å
Ph
Ph2C2 νC-C 1965 cm−1
νC-C 1742 cm−1
1.29 Å
Br
Br
+
Pt(PPh3)3
Na/Hg
– PPh3
Pt
PPh3
PPh3
127°
Ta
Me
Me
Me
Δ 120 °C
– CH4
1.41 Å
1.37 Å
Ta
1.36 Å
1.46 Å
Me
1.41 Å
1.36 Å
Me

Reactions

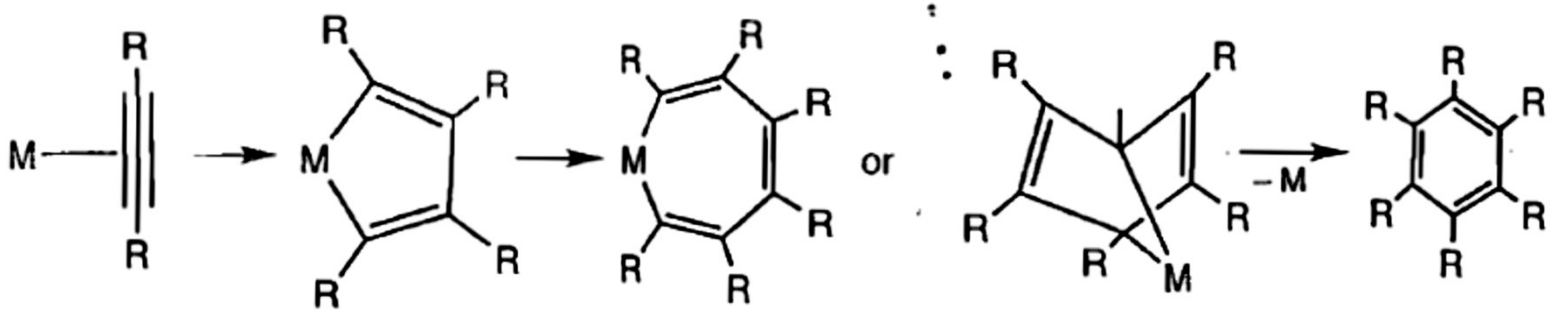


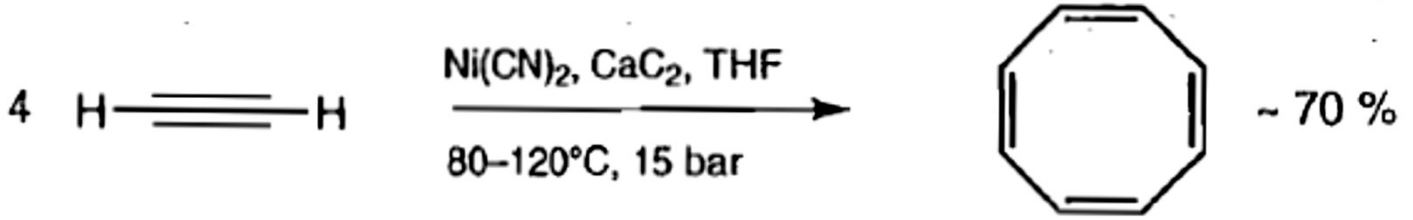
Dimerization of alkynes to anti-aromatic cyclobutadiene with CpCo based reagents

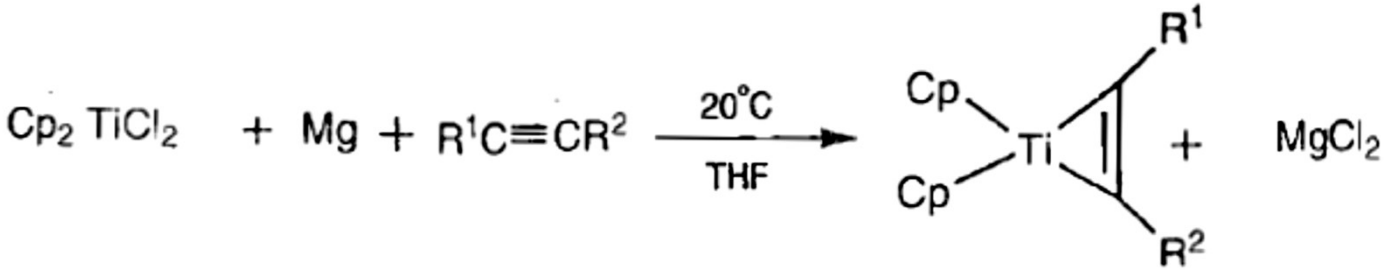


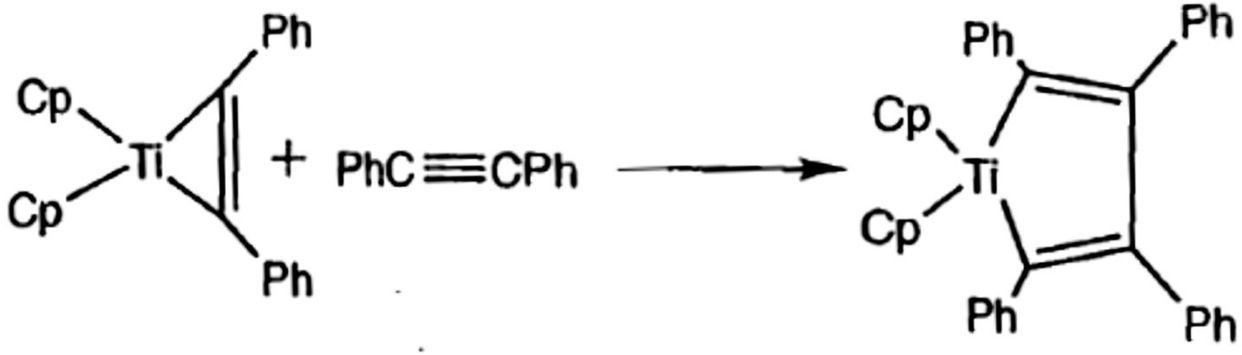


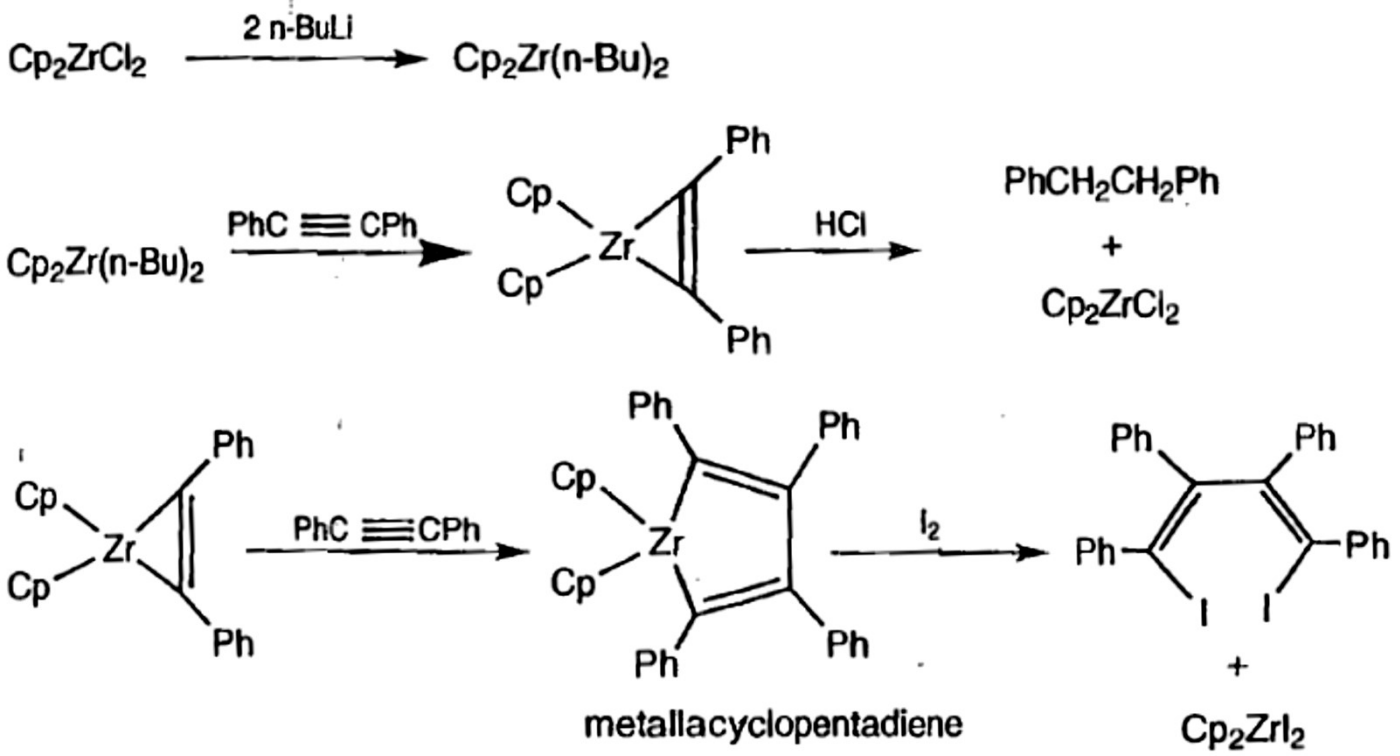
- **Trimerization reaction can also happen with the combination of alkynes with nitriles and their derivatives to give rise to analogues of pyridine.**
- **The attainment of aromaticity is the main driving force for such reactions.**

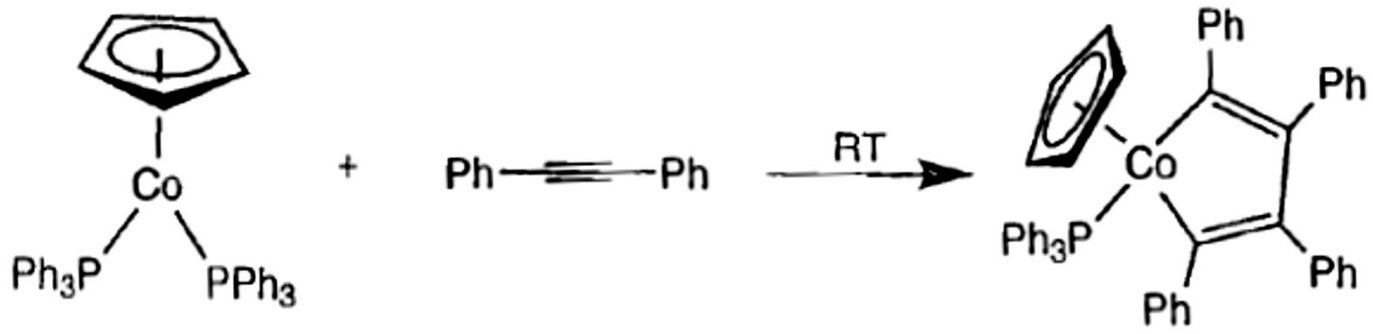

M
R
or
–M


4
H
H
Ni(CN)2, CaC2, THF
80–120°C, 15 bar
~ 70 %


Cp2 TiCl2
+ Mg +
R1C≡CR2
20°C
THF
Cp
Ti
R1
R2
+ MgCl2


Cp
Ti
Ph
+ PhC≡CPh


Cp2ZrCl2
2 n-BuLi
Cp2Zr(n-Bu)2
Cp2Zr(n-Bu)2
PhC ≡ CPh
Cp
Zr
Cp
Ph
Ph
HCl
PhCH2CH2Ph
+
Cp2ZrCl2
Cp
Zr
Cp
Ph
Ph
PhC ≡ CPh
Ph
Ph
Cp
Zr
Cp
Ph
Ph
I2
Ph
Ph
Ph
Ph
I
I
+
Cp2ZrI2
metallacyclopentadiene


Co
Ph3P
PPh3
+
Ph
Ph
RT
Ph
Ph
Co
Ph3P
Ph
Ph
Ph

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**