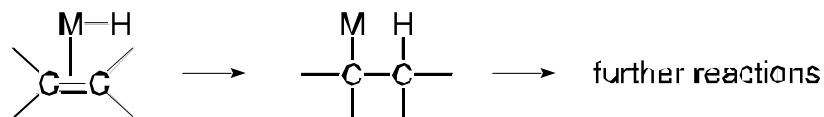


5. The Metal–Carbon π -Bond

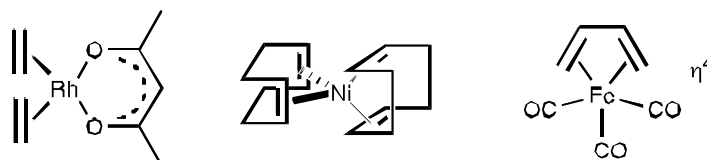
Alkene Complexes and More ...

- Alkene complexes are extremely important because they are the first step of olefin functionalization:



- Virtually all transition metal form olefin complexes – or react with olefins.
- Olefin ligands are soft \rightarrow The ancillary ligands should be soft as well.

Examples:



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Structure of Olefin Complexes

AC 1-Reminder:

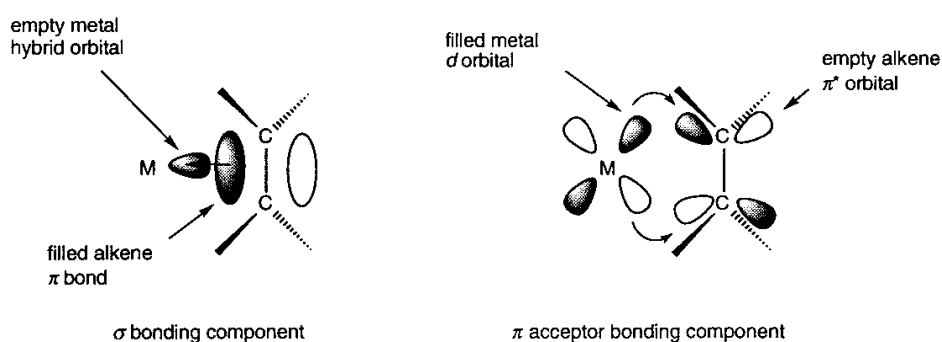


Fig. 6.27. The bonding of an alkene to a metal.

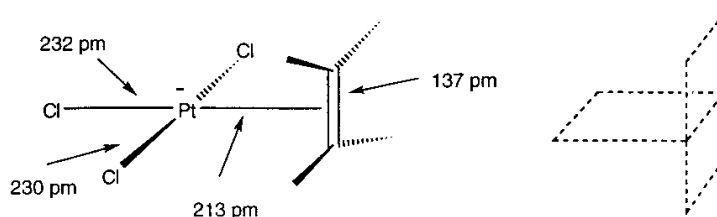


Fig. 6.26. A schematic representation of the structure of Zeise's salt.

(The C–C bond length in non-coordinated ethene is 134 pm.)

Electronic Requirements of the Metal

To form stable olefin complexes, and besides the orbitals of correct symmetry, the metal must possess **high** electron affinity (EA) (for **good σ -accepting properties**) and **low** promotion energy (PE) (for **good π -backbonding**):

Atom or Ion	Ground State	Promotion Energy $d^{10} \rightarrow d^9 s^1$ or $d^8 \rightarrow d^7 s^1$	Promotion Energy $d^{10} \rightarrow d^9 p^1$ or $d^8 \rightarrow d^7 p^1$	Electron Affinity $d^{10} \rightarrow d^{10} s^1$ or $d^8 \rightarrow d^7 s^1$	π -Donor Character	σ -Acceptor Character
Ni(0)	$d^8 s^2$ *	-1.80	1.72	1.2	very good	poor
Pd(0)	d^{10}	0.81	4.23	1.3	good	poor
Pt(0)	$d^9 s^1$	-0.76	3.28	2.4	good	poor
Rh(I)	d^8		1.6	7.31	very good	good
Ir(I)	d^8		2.4	7.95	very good	good
Pd(II)	d^8		3.05	18.56	good	very good
Pt(II)	d^8		3.39	19.42	good	very good
Cu(I)	d^{10}	2.72	8.25	7.72	moderate	good
Ag(I)	d^{10}	4.87	9.94	7.59	moderate	good
Au(I)	d^{10}	1.87	7.83	9.22	poor	good
Zn(II)	d^{10}	9.65	17.1	17.96	poor	very good
Cd(II)	d^{10}	10.0	16.6	16.90	poor	very good
Hg(II)	d^{10}	5.31	12.8	16.90	poor	very good

* Energy of d^{10} -configuration above ground state is 1.80 eV for Ni(0) and 0.76 eV for Pt(0).

Nickel(II) vs. Nickel(0):

Calculated Electron Density on the Olefin

		Ni	C_2H_2	NH_2
$[Ni^{II}(NH_2)_2(C_2H_4)_2]$	Ni(II)	+0.83	+0.02	-0.43
$[Ni^0(NH_3)_2(C_2H_4)_2]$	Ni(0)	+0.58	-0.78	+0.11

In the nickel(II) bis(amido) complex, there is a larger positive charge than in the nickel(0) diamino species.

Nickel(II) is a stronger σ -acceptor and weaker π -donor than nickel(0).

→ Effect on reactivity!

(B. Åkermark, M. Almemark, J. Almlöf, J. E. Bäckvall, B. Roos, Å. Støgard, *J. Am. Chem. Soc.* **1977**, 99, 4617.)

Effect of Olefin Coordination on the C=C Bond Length

Both the σ -donation from the olefin ($M \leftarrow \sigma$ -olefin) and the π -backdonation from the metal ($M \xrightarrow{\pi}$ -olefin) weaken the C=C bond, as indicated by the $\nu(\text{C}=\text{C})$ vibrational frequencies:

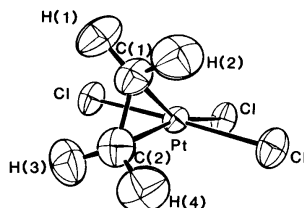
	$\nu(\text{C}=\text{C}) / \text{cm}^{-1}$
$[\text{Rh}(\text{Cp})(\text{C}_2\text{H}_4)_2]$	1493
$[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$	1506
$[\text{Mn}(\text{Cp})(\text{C}_2\text{H}_4)(\text{CO})_2]$	1508
$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	1516
$[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$	1525
$[\text{Fe}(\text{Cp})(\text{C}_2\text{H}_4)(\text{CO})_2]\text{PF}_6$	1527
$[\text{Re}(\text{C}_2\text{H}_4)_2(\text{CO})_4]\text{PF}_6$	1539
$[\text{Fe}(\text{C}_2\text{H}_4)_2(\text{CO})_4]$	1551
$[\text{Ag}(\text{C}_2\text{H}_4)_2]\text{BF}_4$	1584
free $\text{H}_2\text{C}=\text{CH}_2$	1623

Strong effect of the ancillary ligands!

Not diagnostic of charge distribution!

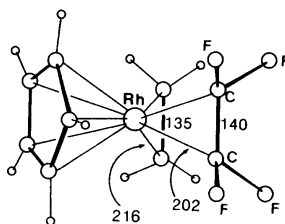
Structural Aspects

Loss of planarity of the olefin upon coordination to a transition metal:



Structure (neutron diffraction) of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$. The C-C bond length is 137 pm, similar to the uncomplexed olefin (135 pm). The olefin is oriented perpendicular to the PtCl_3 -plane. The Pt-Cl bond trans to the olefin is slightly elongated. The atoms H(1)-H(4), C(1) and C(2) are not coplanar. The dihedral angle between the CH_2 planes is 146° (Bau, 1975).

In substituted ethylenes C_2X_4 , this deformation increases with increasing electronegativity of X:

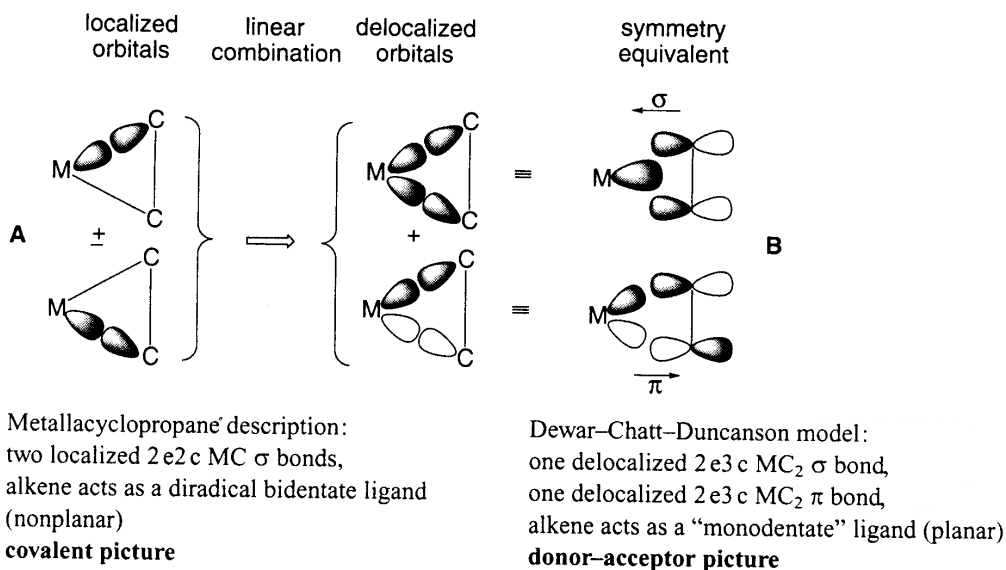


Structure (X-ray diffraction) of $(\text{C}_6\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$. The carbon atoms of C_2F_4 are closer to the metal than those of C_2H_4 . The dihedral angle between the two CH_2 -planes in C_2H_4 is 138° , that of the CF_2 -planes in C_2F_4 is 106° (Guggenberger, 1972).

Is this an indication of a "metallacyclopropane" structure?

Dewar-Chatt-Duncanson or Metallacyclopropane?

The actual bonding situation is somewhere between these two limiting cases:



Whereas in the limiting case **B** the carbon atoms are sp^2 -hybridized (planar η^2 -ethylene, long M–C, short C=C), in limiting case **A** the percentage of p character in the hybrid orbitals is higher (non-planar η^2 -ethylene, short M–C, long C=C). The deviation from planarity of coordinated ethylene should therefore correlate with the tendency of the C atoms to form hybrid orbitals with higher p character. This tendency grows with increasing electronegativity of their substituents (Bent's rule: as a representative example, the $CH_3\cdot$ radical is planar (sp^2), whereas $CF_3\cdot$ is pyramidal (sp^3)).

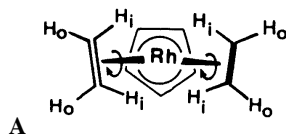
^{13}C NMR Spectroscopy

^{13}C NMR chemical shifts are indicative of the degree of pyramidalization of the olefin C atoms:

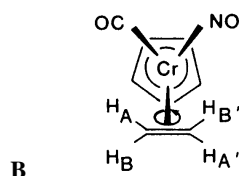
	$\delta(^{13}C)$	
1,5-cyclooctadiene	128.6	
[PdCl ₂ (1,5-COD)]	117.2	
[PtCl ₂ (1,5-COD)]	100.6	
[RhCl(1,5-COD)] ₂	78	
[IrCl(1,5-COD)] ₂	62.1	stronger M–olefin bond, enhanced sp^3 character

Hindered Olefin Rotation

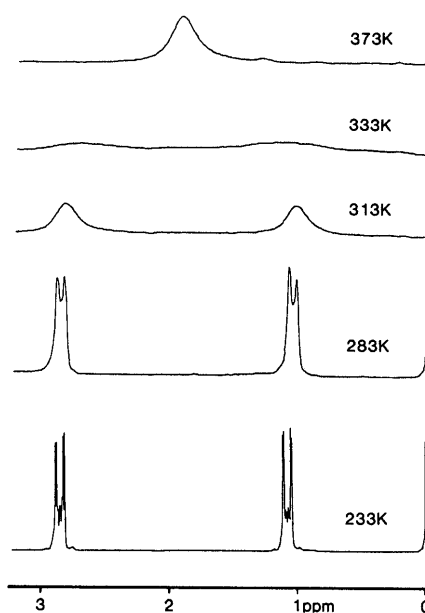
This dynamic process often occurs in a temperature range that is suitable for routine ^1H and ^{13}C NMR studies, as shown for $[\text{Rh}(\text{Cp})(\text{C}_2\text{H}_4)_2]$ (**A**). On fast rotation around the Rh-ethylene axis (the rotational frequency is higher than the signal separation in Hz), the inner (H_i) and outer (H_o) protons appear equivalent. At low temperatures, the rotation is "frozen" and an AA'XX' spectrum is observed instead of a single signal (see spectrum on the right):



The temperature-dependent ^1H NMR spectrum of the chiral complex $[\text{Cr}(\text{Cp})(\text{C}_2\text{H}_4)(\text{CO})(\text{NO})]$ (**B**) rules out that rotation takes place around the C–C axis of ethylene:

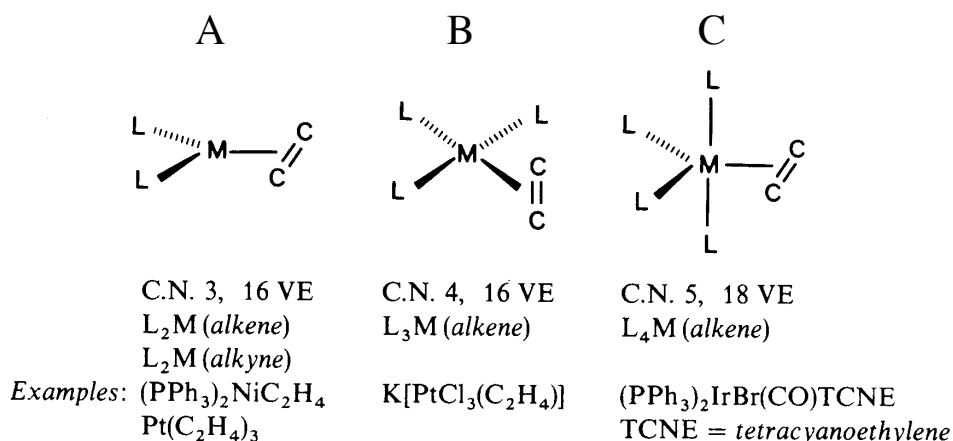


Upon raising the temperature, the spectrum of **B** converts from an ABCD to an AA'BB' type. Two pairs of diastereotopic protons are therefore retained. An additional rotation around the ethylene (C–C) axis would result in an A_4 -type spectrum.



^1H -NMR spectrum of $\text{C}_2\text{H}_3\text{Rh}(\text{C}_2\text{H}_4)_2$ (200 MHz).

Conformation Relative to the Metal–Olefin Axis



The olefin tends to lie in the trigonal plane in complexes of type **A** and **C** for electronic reasons.

In the case of complexes of type **B**, both conformations have similar energy, and the orientation perpendicular to the plane of the molecule is favored for steric reasons.

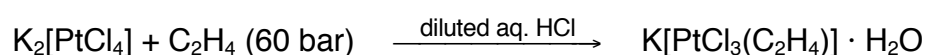
(see next exercise)

Synthesis of Alkene Complexes

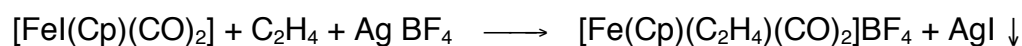
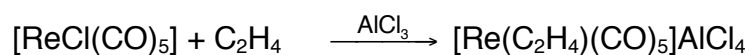
1. Substitution reactions
2. Addition reactions
3. Metal salt + olefin + reducing agent
4. Metal-atom ligand-vapor cocondensation
5. Nucleophilic attack onto enyl complexes
6. β -Hydrogen abstraction from alkyl complexes

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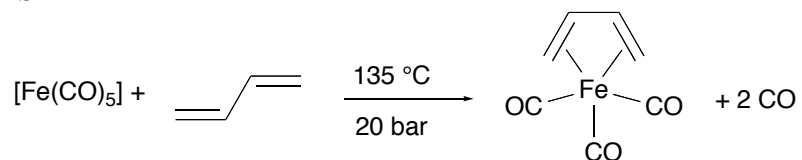
1. Substitution Reactions



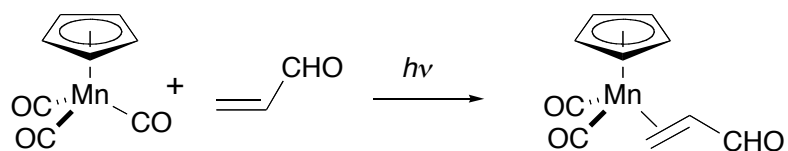
- Substitution of a halo (chloro, iodo) ligand is promoted by a "chloride scavenger" that either produces a non-coordinating anion (AlCl_3 to AlCl_4^-) or forms an insoluble halide salt:



- Thermal Ligand Substitution:

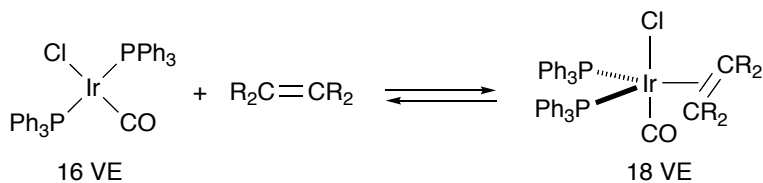


- Photochemical Ligand Substitution (proceeds at low temperatures):

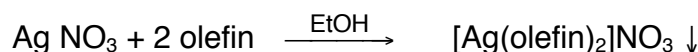


2. Addition Reactions

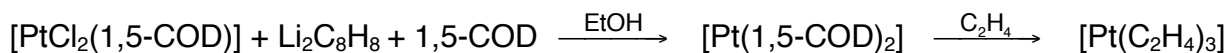
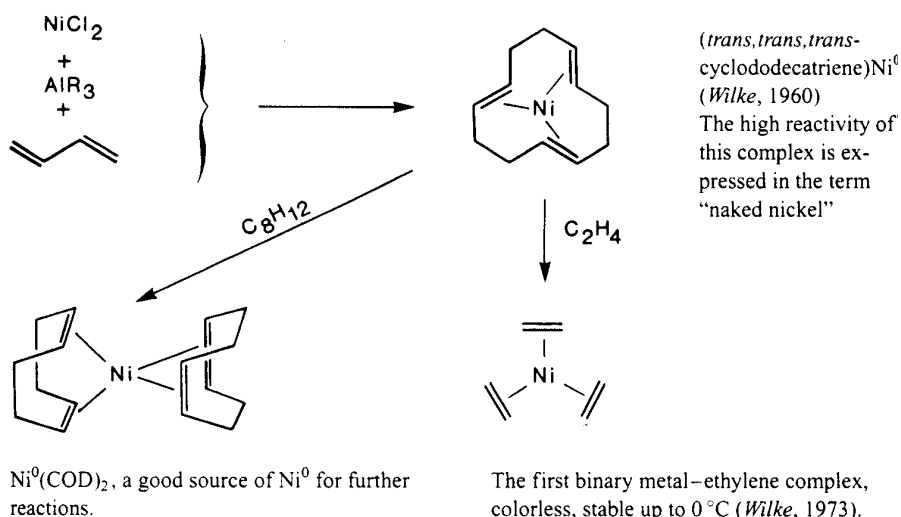
Coordinationally unsaturated complexes can add olefin ligands without replacement of another group (addition):



A simple method for the separation of isomeric olefins by recrystallization of their silver nitrate adducts is based on the following equilibrium:

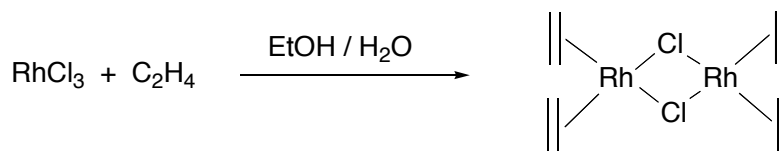


3a. Metal Salt + Olefin + (Strong) Reducing Agent



Tris(ethylene)platinum(0) is only stable under an atmosphere of C_2H_4 !

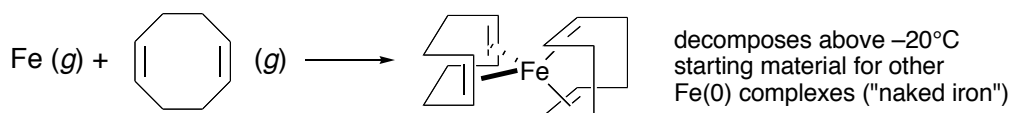
3b. Metal Salt + Olefin + (Weak) Reducing Agent



Rhodium is reduced by excess ethylene. How?

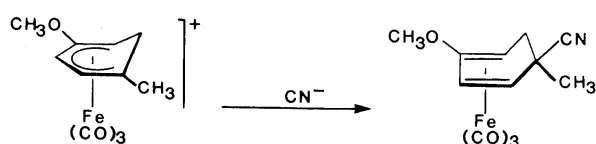
4. Metal-Atom Ligand-Vapor Cocondensation (Or Metal-Vapor Synthesis)

Metal atom vapors are condensed with gaseous ligand or into a ligand solution of low vapor pressure on a cooled surface. Upon warming to room temperature, metal complexes are formed in competition with metal aggregation.



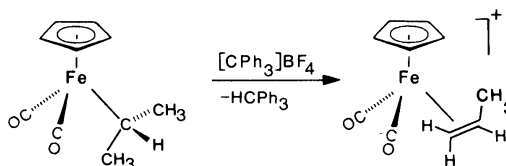
Cocondensation techniques currently represent the only method of accessing several fundamental organometallic compounds. Drawbacks of this method include the frequently low yields and the large amounts of cooling agent required.

5. Nucleophilic Attack onto Enyl Complexes

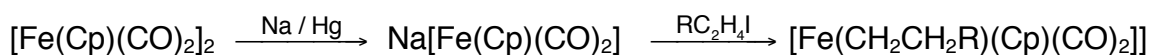


Such nucleophilic additions are generally regio- and stereoselective and take place in the *exo* orientation.

6. β -Hydrogen Abstraction from Alkyl Complexes



Synthesis of the alkyl complex (must bear a β -H atom):



The Reactivity of Olefin Complexes

We will consider the following reaction types:

1. Substitution reactions with olefin loss
2. Substitution reactions without olefin loss
3. Nucleophilic attack onto the olefin (Wacker)

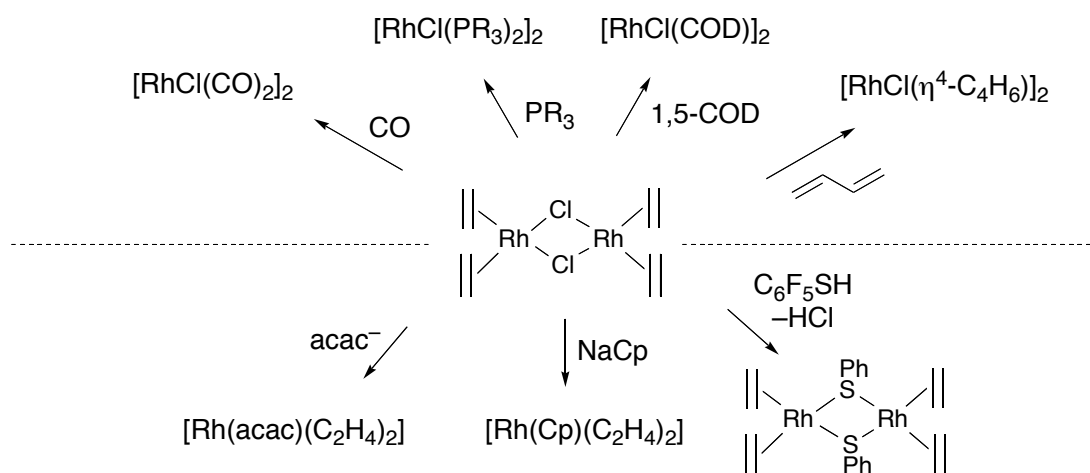
The most important metallorganic reactions of alkene complexes:

4. Olefin insertion into M...H and M–C bonds has been discussed in the chapter on alkyl complexes.
5. Olefin metathesis by carbene complexes will be discussed in the next chapter.

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1. Substitution Reactions with Loss of Olefin

Alkene complexes can be used as labile precursors, because monodentate olefins are readily substituted by dienes (chelate effect) or by strong π -acceptors (without M–Cl cleavage):

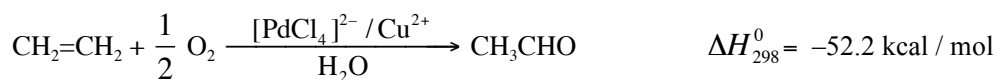


2. Substitution Reactions without Loss of Olefin

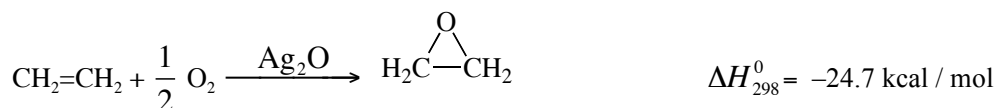
In contrast, soft anions promote chloride substitution. In general, such anions are π -donors and the stabilization caused by the push-pull interaction between the olefin and the anion drives the reaction.

3. The Wacker Process: Olefin Oxidation

Thermodynamics:



$$\Delta G_{298}^0 = -48.2 \text{ kcal / mol}$$

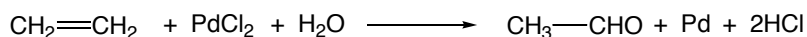


$$\Delta G_{298}^0 = -19.1 \text{ kcal / mol}$$

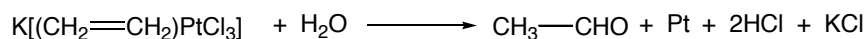


$$\Delta G_{298}^0 = -314.1 \text{ kcal / mol}$$

Some Preliminary Observations:



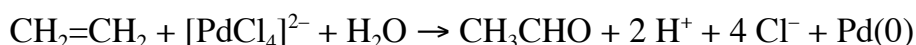
F. C. Phillips, *Am. Chem. J.* **1894**, 16, 255.



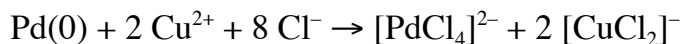
J. S. Anderson, *J. Chem. Soc.* **1934**, 971.

Single Steps

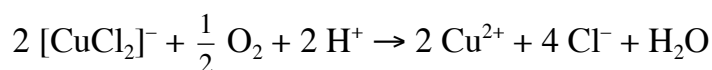
Ethene is converted to acetaldehyde in the presence of tetrachloropalladate(2-) and water.



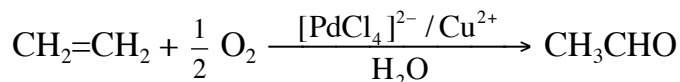
Ethene is oxidized, palladium(II) is reduced to palladium(0). Therefore, palladium can be used as catalyst in the presence of an oxidant whose E_{red}^0 is more positive than $E^0(\text{Pd(II)}/\text{Pd(0)})$. Such an oxidant will reoxidize Pd(0) to Pd(II):



An appropriate oxidant is O_2 :

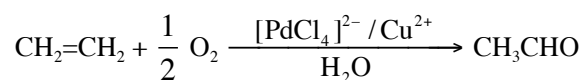


The sum is:



Rate Law

The reaction



has the rate law

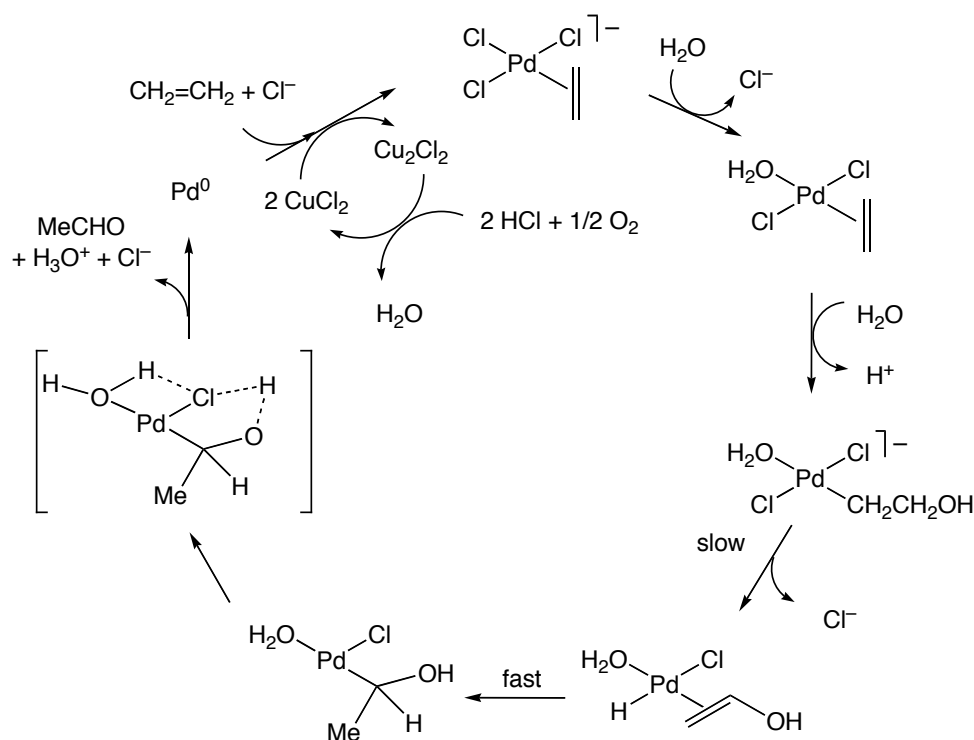
$$r = k_{\text{obs}} \frac{[\text{PdCl}_4^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2[\text{H}^+]}$$

under the following conditions: $[\text{Pd}^{2+}] = 0.005 - 0.04 \text{ M}$; $[\text{Cl}^-] = 0.1 - 1 \text{ M}$; $[\text{H}^+] = 0.04 - 1 \text{ M}$.

Hydroxyalkyl Intermediate:



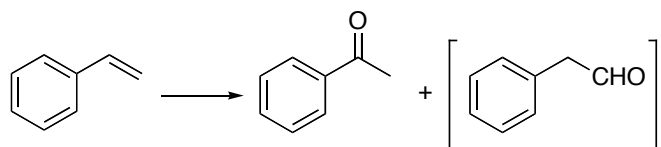
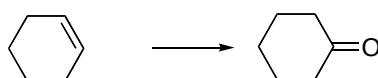
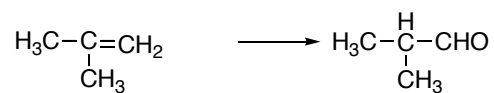
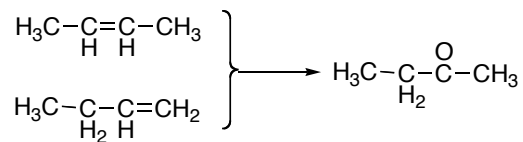
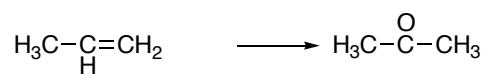
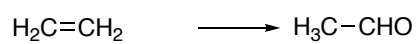
Wacker Process



Transition state suggested in a theoretical study: J. A. Keith, J. Oxgaard, W. A. Goddard III, *J. Am. Chem. Soc.* **2006**, 128, 3132.

Selectivity of the Wacker Process

(In aqueous solution)



η^2 -, η^4 -, and η^6 -Arene Ligands

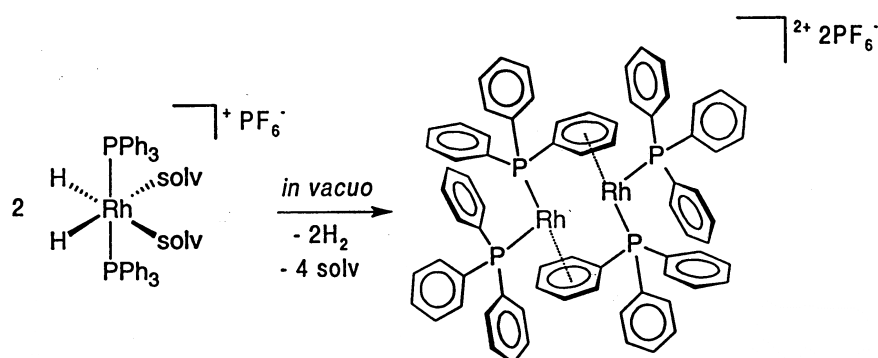
Arenes can bind in a π -fashion to a metal center.

Several Rh(I) complexes are known.

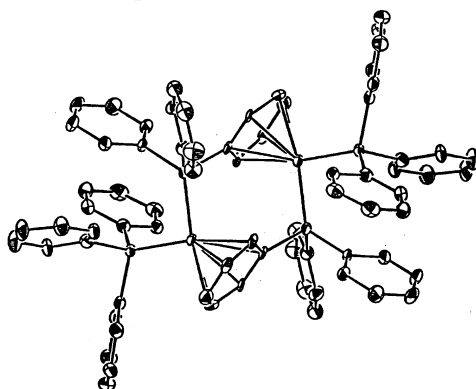
1. η^6 -Arene Ligands in complexes of d^8 and d^6 metals

2. η^2 -Arene Ligands

η^6 -Arene Ligands

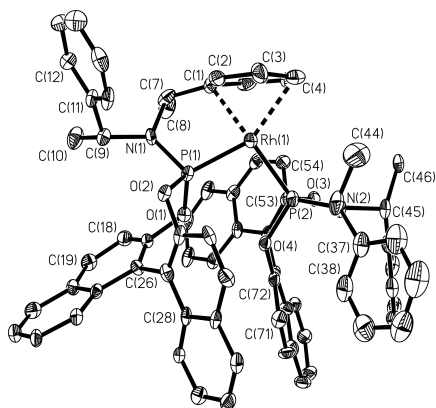
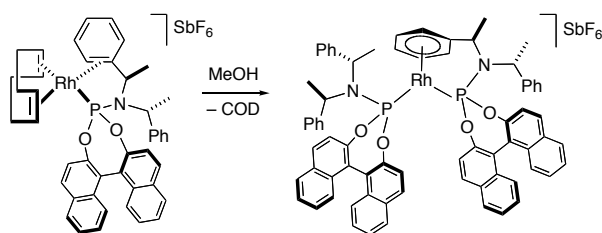


X-Ray Structure of the Dicationic Binuclear Complex:



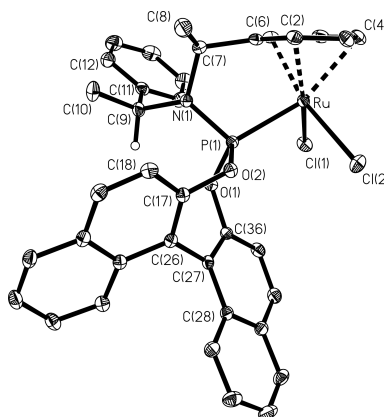
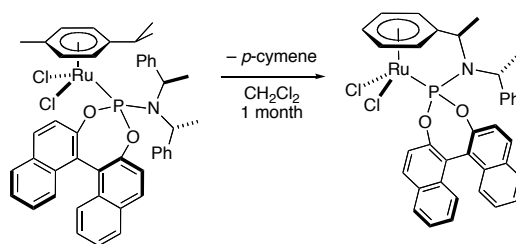
η^6 -Arene Complexes

d^8



Ru–C(phenyl) (average): 2.33 Å

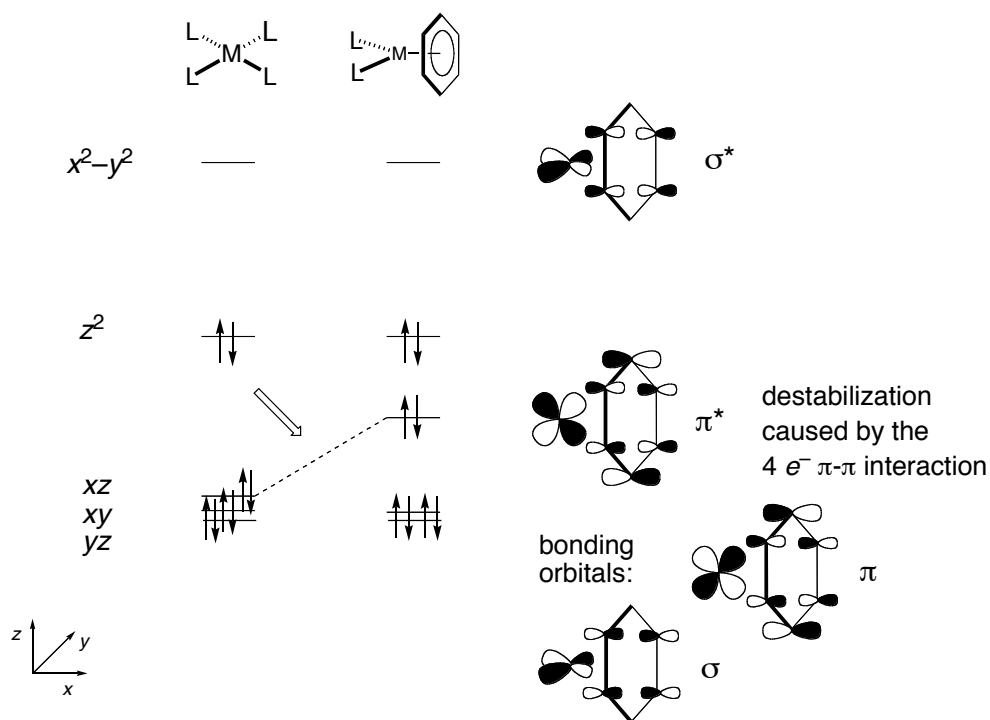
d^6



Ru–C(phenyl) (average): 2.21 Å

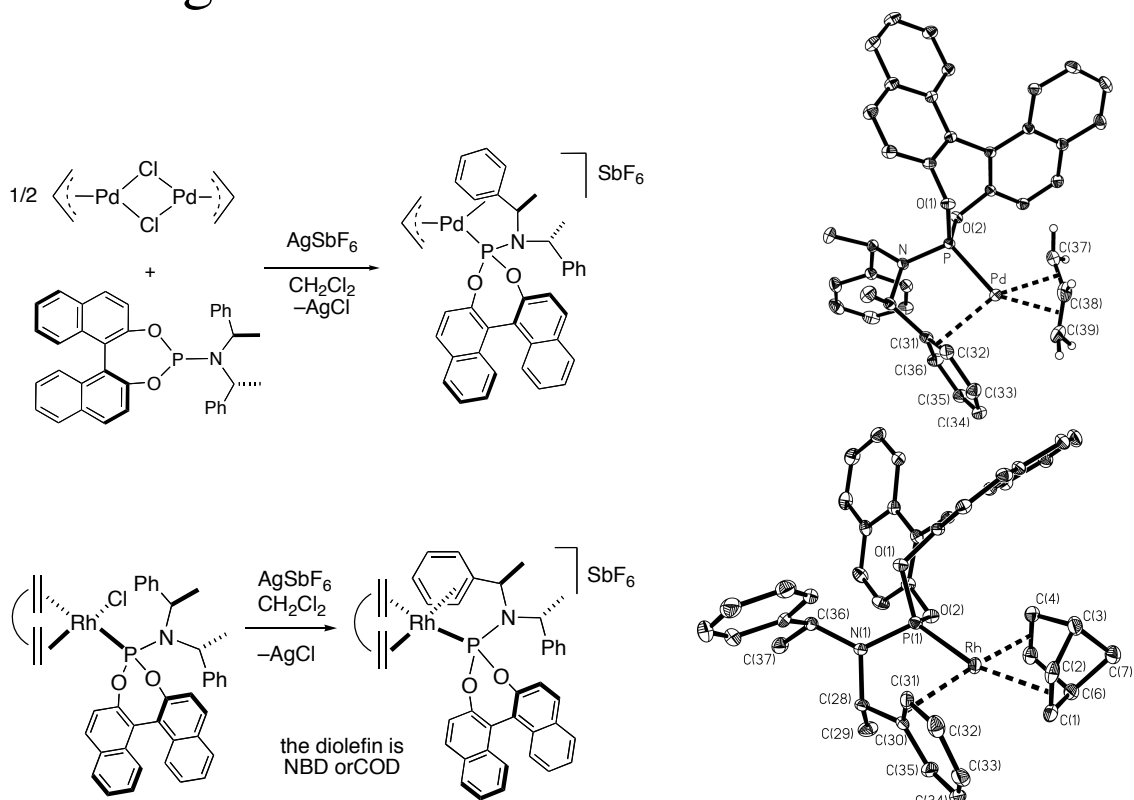
I. S. Mikhel, H. Rüegger, P. Butti, F. Camponovo, D. Huber, A. Mezzetti, *Organometallics*, **2008**, 27, 2937.

η^6 -Arene Complexes of d^8 Metals: Is the Arene a 6-Electron Donor?



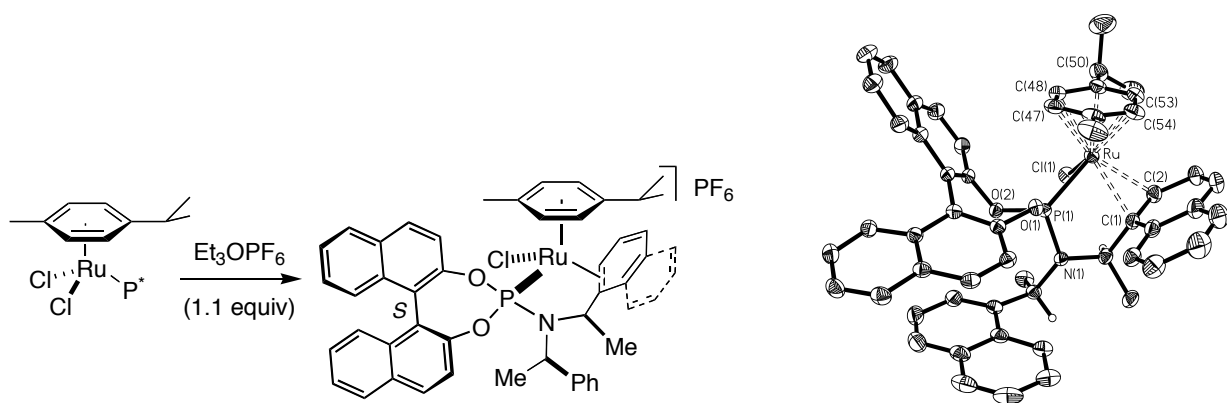
See: E. L. Muetterties, J. R.; Bleeke, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982**, 82, 499.

η^2 -Arene Ligands: d^8 Metals



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η^2 -Arene Ligands: d^6 Metals



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