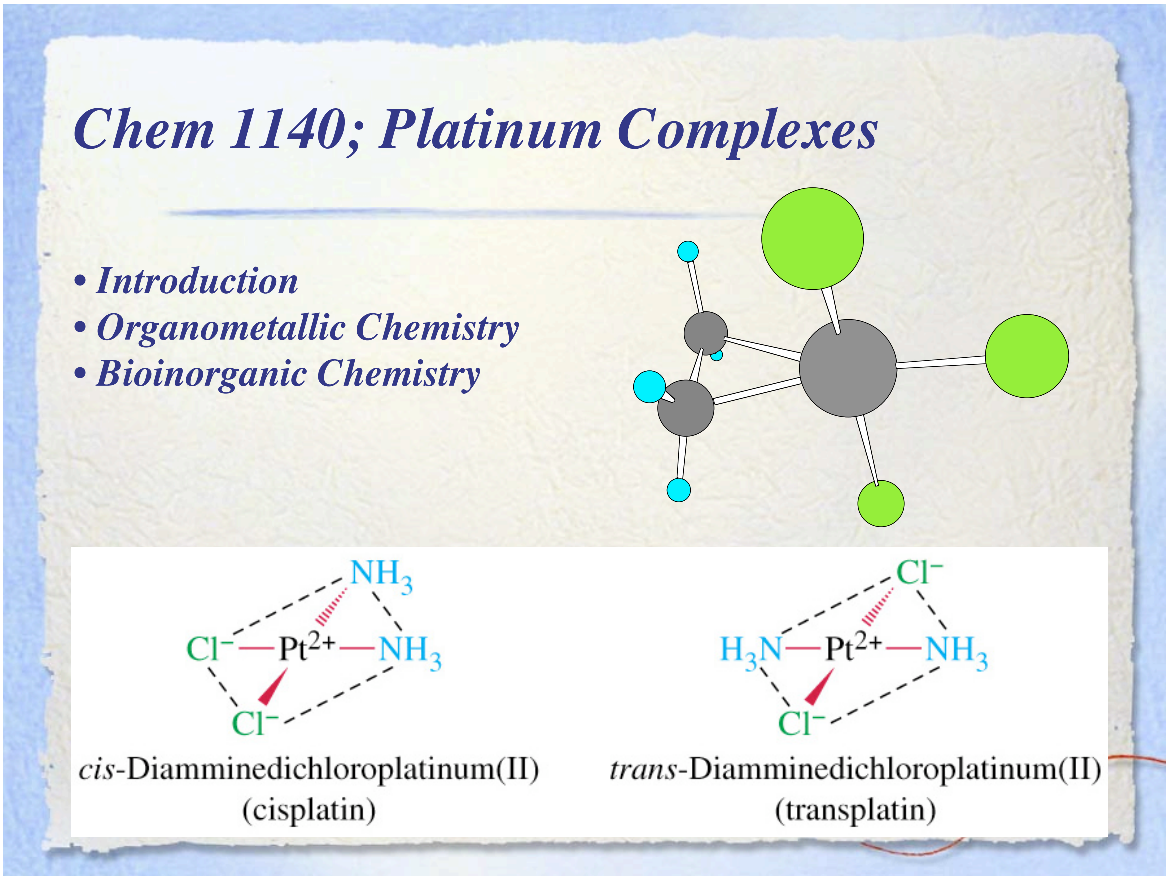
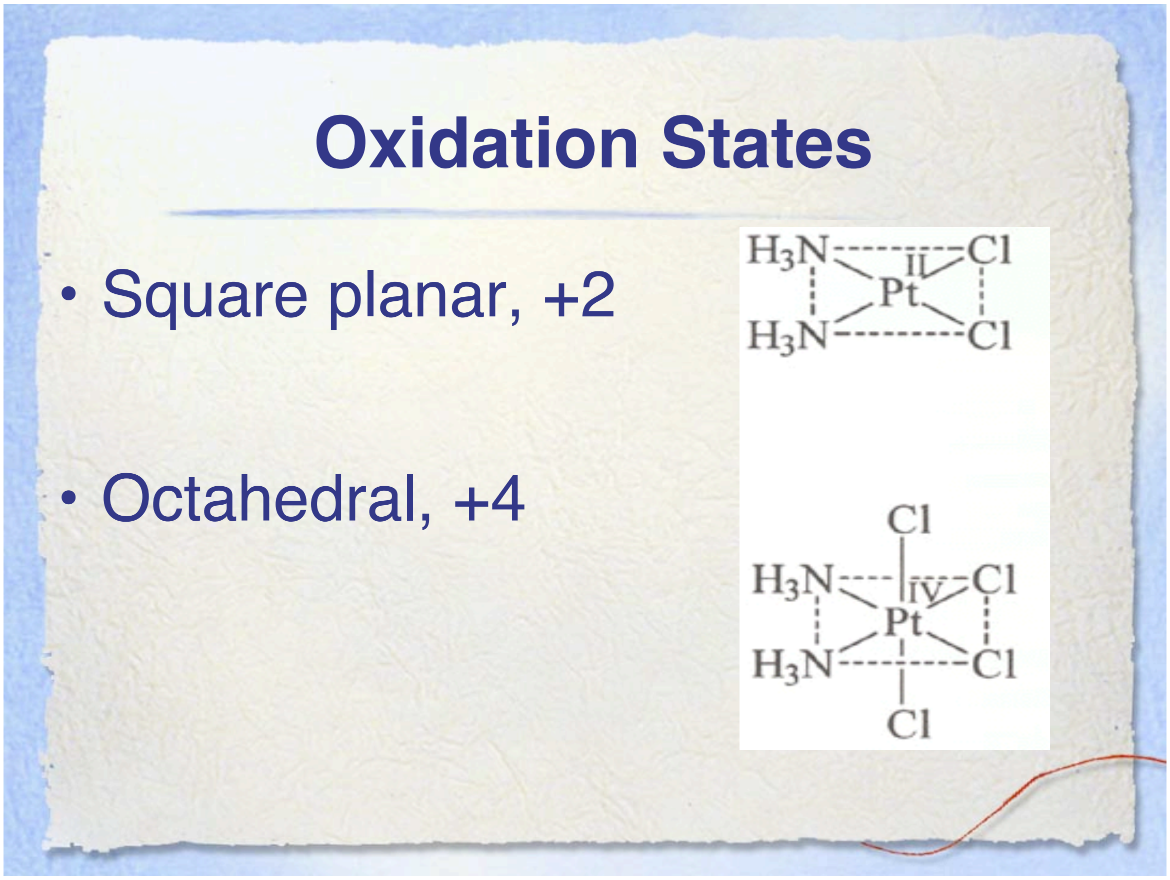


Chem 1140; Platinum Complexes

- ***Introduction***
- ***Organometallic Chemistry***
- ***Bioinorganic Chemistry***

cis-Diamminedichloroplatinum(II)
(cisplatin)

trans-Diamminedichloroplatinum(II)
(transplatin)

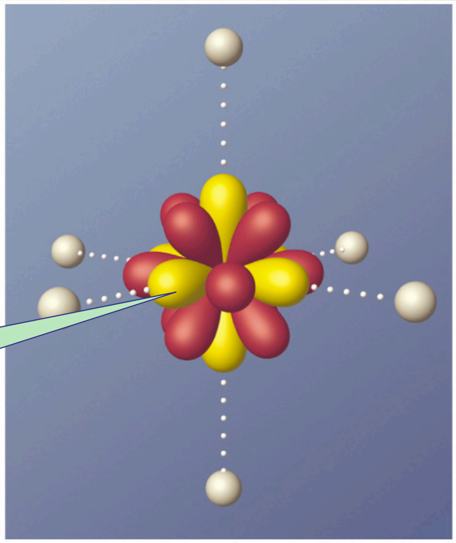


Oxidation States

- Square planar, +2
- Octahedral, +4

Bonding in Complexes: Crystal Field Theory

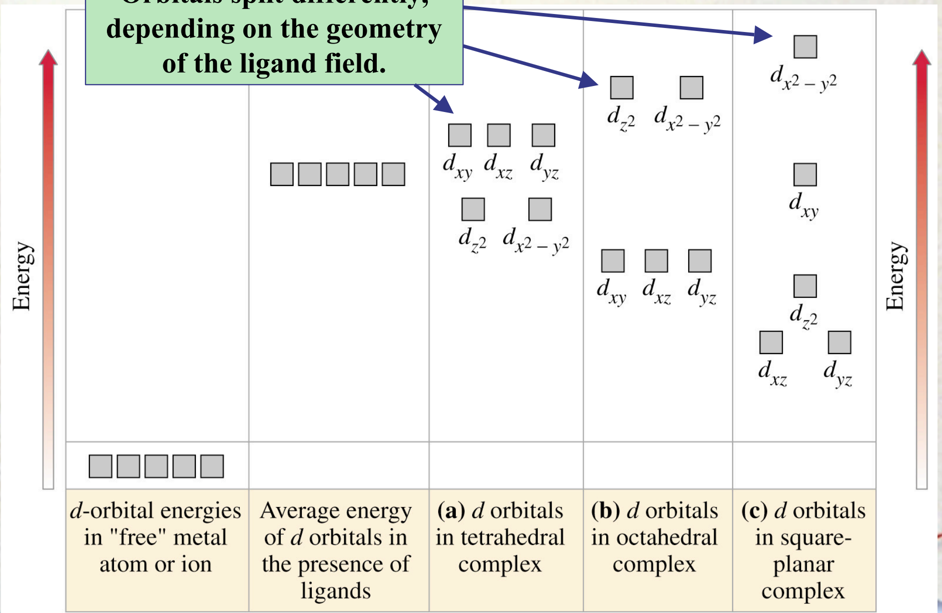
- Attractions between a central atom or ion and its ligands are largely electrostatic.
- Ligands can distort the *d*-orbitals of the central species, leading to a *splitting* of energy levels of those orbitals.



Orbitals in yellow will be *higher* in energy than orbitals in red, due to the octahedral ligand field.

Bonding in Complexes: Crystal Field Theory

Orbitals split differently, depending on the geometry of the ligand field.



General Remarks on Platinum Complexes

- Principles oxidation states of Pt are II and IV; with phosphine and CO ligands, 0 oxidation states are also stabilized.
- The II state is d^8; these Pt(II) is almost invariably square-planar and are most frequently of the type MX_2L_2 (X=monodentate anion, L=donor ligand), which may exist as *cis* and *trans* isomers).
- Pt(II) shows low affinity for hard (F^- and O) ligands and a preference for heavier halogens and ligands that can p-bond, such as R_3P, R_2S, CN^-, alkenes and alkynes.
- The kinetic inertness of Pt(II) (and Pt(IV) complexes allowed them to play an important role in the development of coordination chemistry such as studies of geometrical isomerism and reaction mechanism.

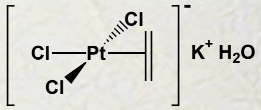
General Remarks on Platinum Complexes

- The IV state is d^6; These Pt(IV) are mostly octahedral, with a coordination number of 6.
- The substitution reactions of Pt(IV) complexes are greatly accelerated by the presence of Pt(II) species.

Acidities of common transition metal hydrides

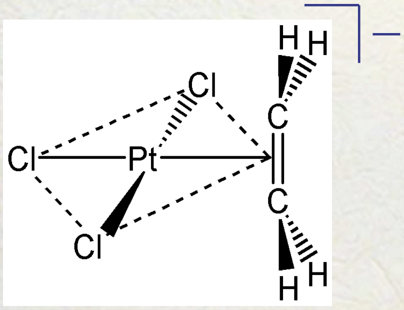
	pKa		pKa
$HV(CO)_6$	strong	$H_2Ru(CO)_4$	11.2
$HV(CO)_5PPh_3$	6.8	$HRuCp(CO)_2$	12.7
$HCrCp(CO)_3$	5.4	$H_2Os(CO)_4$	13.3
$HMoCp(CO)_3$	6.2	$HCo(CO)_4$	strong
$HWCp(CO)_3$	8.0	$HCo(CO)_3(PPh_3)$	7.0
$HMn(CO)_5$	7.1	$HCo(CO)_3(P(OPh)_3)$	4.9
$HMn(CO)_4(PPh_3)$	12.9	$HCo(CO)_2(PPh_3)_2$	very weak
$HRe(CO)_5$	13.6	$HNi[P(OPh)_3]_4^+$	5.9
$H_2Fe(CO)_4$	4.4	$HPd[P(OPh)_3]_4^+$	3.1
$HFeCp(CO)_2$	11.9	$HPt[P(OPh)_3]_4^+$	11
$HFeCp^*(CO)_2$	18.8		

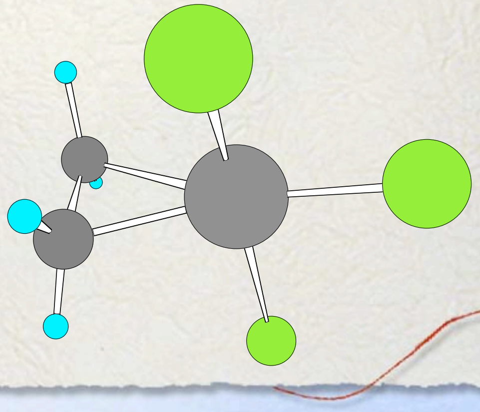
Zeise's Salt



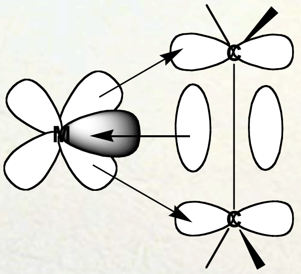
W. C. Zeise $PtCl_2(C_2H_4)•KCl•H_2O$ 1827

The history of organometallic chemistry began with Zeise's salt in 1827 when reacting $PtCl_4$ and $PtCl_2$ in refluxing ethanol.





$$[PtCl_4]^{2-} + H_2C{=}CH_2 \xrightarrow{HCl} [Pt(C_2H_4)Cl_3]^- + Cl + H_2O$$



$LRh(C_2H_4)(C_2F_4)$

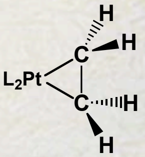
L: acetylacetonate
cyclopentadienyl

Rh—C 217-219 pm

Rh—C 201-202 pm

$C_2F_4 > C_2H_4$ π-accepting ability

$Pt(PPh_3)_2(CH_2{=}CH_2)$



The extent of back bonding varies, depending on the metal, the substituents on ethylene, and other ligands on the metal.

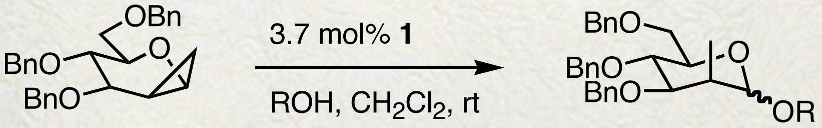
Di-μ-chlorodichlorobis(η²-ethene)diplatinum, Zeise's Dimer

(1)

- Reagent for cyclopropane isomerization and cleavage, synthesis of platinacyclobutanes, hydration of alkynes.

Ring-Opening of Cyclopropanes

Platinum complexes, including the title reagent, react readily with cyclopropanes to form platinacyclobutanes. If cyclopropane is oxygenated then a variety of products can be obtained. Sugar-derived cyclopropanes undergo opening with trapping by alcohols in presence of Zeise's dimer **1** (eqs 1 and 2). Water and phenols are also active nucleophiles for this transformation, and some substituted cyclopropanes can also be used.



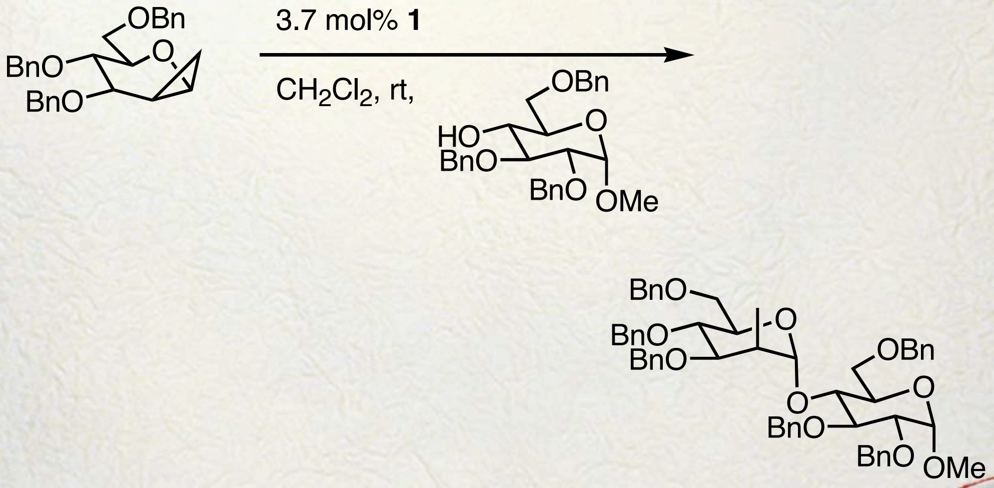
(1)

MeOH: 82%, 21:1 (α:β)
BnOH: 95%, 12:1 (α:β)
allylOH: 92%, α only
t-BuOH: 53%, 9:1 (α:β)

Di-μ-chlorodichlorobis(η^2-ethene)diplatinum, Zeise's Dimer

(1)

Ring-Opening of Cyclopropanes



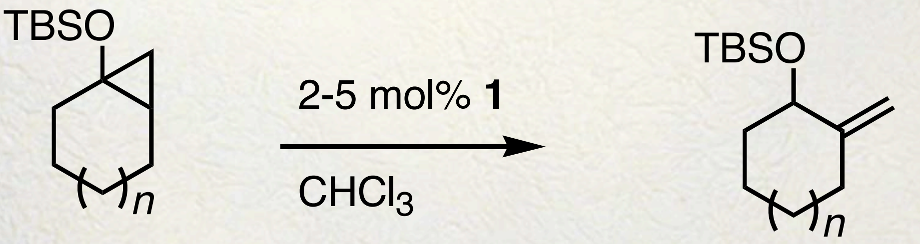
(2)

Di-μ-chlorodichlorobis(η^2-ethene)diplatinum, Zeise's Dimer

(1)

Ring-Opening of Cyclopropanes

Silyloxycyclopropanes, including cyclopropanes fused to another ring, are readily isomerized to 2-methylene alkanols by catalytic amounts of **1** (eq 4).



(4)

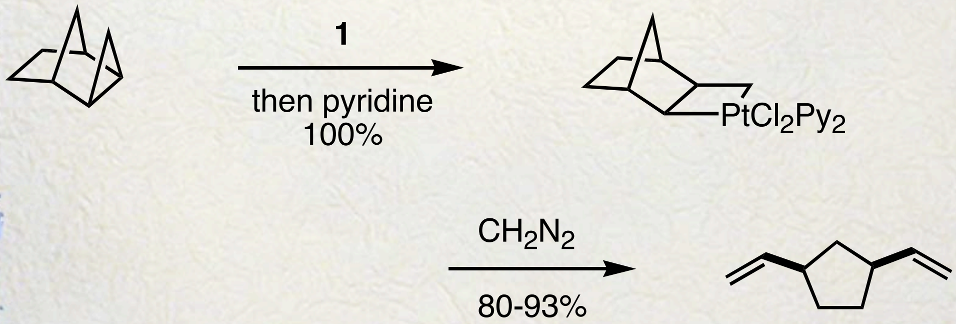
$n = 1$, 96%
$n = 2$, 96%
$n = 4$, 73%

Di-μ-chlorodichlorobis(η^2-ethene)diplatinum, Zeise's Dimer

(1)

Synthesis of Platinacyclobutanes

Zeise's dimer can also be used to synthesize platinacyclobutanes from cyclopropanes. Platinacyclobutanes are often stable compounds, and undergo a variety of transformations, including ring opening with diazomethane to give alkenes (eq 5), olefins by β-hydride abstraction and reductive elimination, and ring expansion to give platinacyclopentanes.



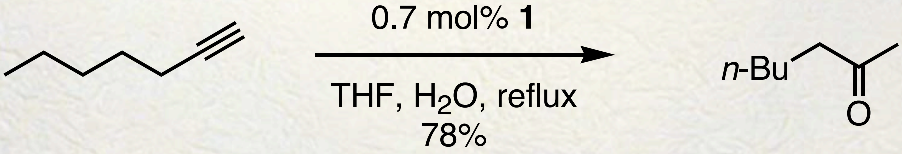
(5)

Di-μ-chlorodichlorobis(η^2-ethene)diplatinum, Zeise's Dimer

(1)

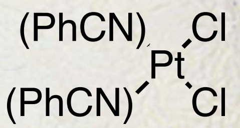
Catalytic Hydration of Alkynes

Zeise's dimer **1** can be used to hydrate alkynes (eq 6). Non-symmetrical internal alkynes give mixtures of products.



(6)

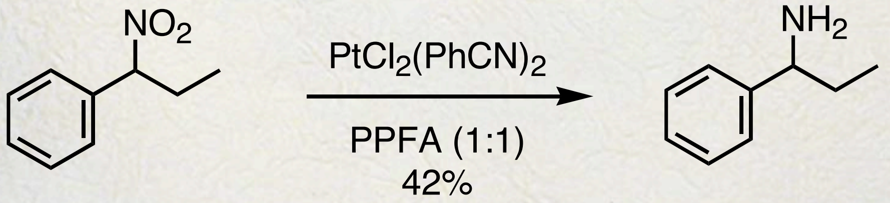
Bis(benzonitrile)dichloroplatinum (II)



Catalyst for hydrogenation of nitro compounds and hydroformylation of alkenes; versatile starting material for complexes of platinum. The labile ligand, PhCN, can be easily displaced with various phosphorus(III) ligands, thereby modifying or improving the activity of the catalyst.

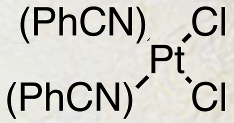
Hydrogenations

The homogeneous hydrogenation of aliphatic nitro compounds is catalyzed by platinum metal phosphine complexes. These complexes are formed in situ by treating the title reagent, which possesses the labile ligand PhCN, with a phosphine reagent, for example (R)-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) at 1000 psi.

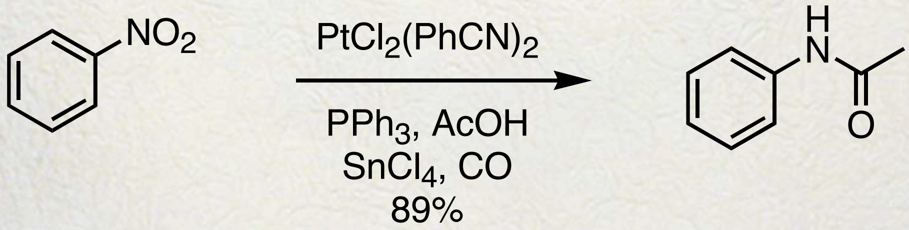


(1)

Bis(benzonitrile)dichloroplatinum (II)

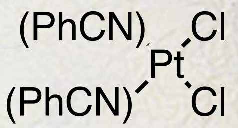


These catalysts have also been utilized in the reductive *N*-acylation of nitro compounds. The catalyst system requires the **platinum** catalyst, carbon monoxide, a Lewis acid (***tin(IV) chloride***), and a phosphorus(III) ligand. For example, the title reagent, when used in conjunction with ***triphenylphosphine***, SnCl4, acetic acid, and CO at 60 atm, yields acetanilide in 89% yield from nitrobenzene (eq 2). When ethanol is used in place of the acetic acid, the resulting product is the carbamate.



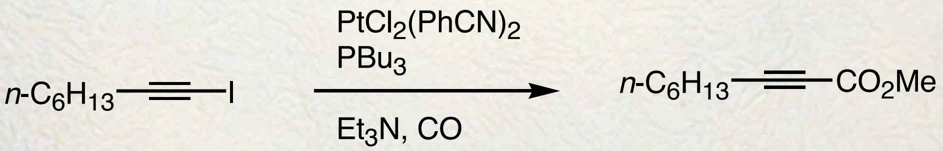
(2)

Bis(benzonitrile)dichloroplatinum (II)



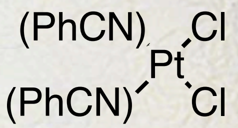
Carbonylations, Rearrangements, and *N*-Alkylations

These catalysts have been used for the carbonylation of alkyl, alkenyl, and alkynyl iodides under carbon monoxide pressure. The title reagent, when used in the presence of ***tri-n-butylphosphine*** and ***triethylamine***, shows good catalytic activity in the methoxycarbonylation of 1-iodo-1-octyne (eq 3).



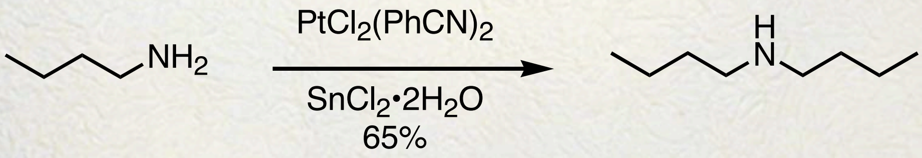
$$n\text{-}C_6H_{13}C{\equiv}C{-}I \xrightarrow[\text{Et}_3\text{N, CO}]{\text{PtCl}_2(\text{PhCN})_2,\ \text{PBu}_3} n\text{-}C_6H_{13}C{\equiv}C{-}CO_2Me \quad (3)$$

Bis(benzonitrile)dichloroplatinum (II)



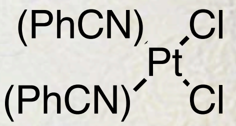
Carbonylations, Rearrangements, and *N*-Alkylations

The transformation of a primary amine to a secondary amine has also been catalyzed by the title reagent. In the presence of the Lewis acid SnCl2.2H2O (Sn:Pt = 2.5:1), it catalyzes the reaction of *n*-butylamine to give *N,N*-dibutylamine in 65% yield (eq 4).



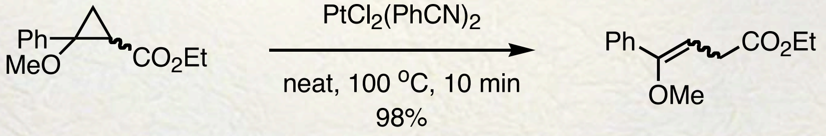
(4)

Bis(benzonitrile)dichloroplatinum (II)



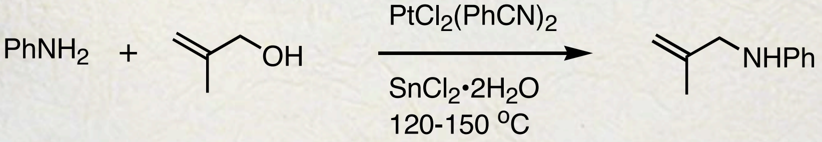
Carbonylations, Rearrangements, and *N*-Alkylations

The rearrangement of cyclopropanes containing the combination of vicinal alkoxy and alkoxycarbonyl substituents is facile when using $PtCl_2(PhCN)_2$ as the catalyst (eq 5).



(5)

N-Alkylation and *N*-allylation can be catalyzed with $PtCl_2(PhCN)_2$ in conjunction with $SnCl_2$•$2H_2O$. Reaction of aniline with an allylic alcohol gives *N*-allylated products (eq 6).



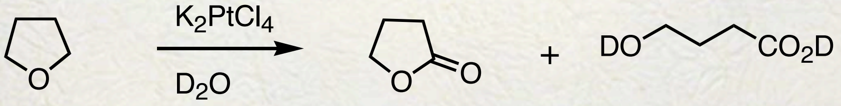
(6)

Dipotassium Tetrachloroplatinate(II), K_2PtCl_4

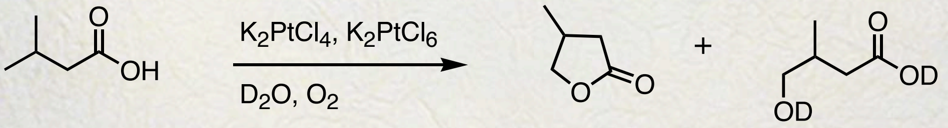
Homogeneous hydrogen isotope exchange catalyst; selective oxidative functionalization of alkane C-H bonds; used for the synthesis of various platinum complexes

Functionalization of Saturated Hydrocarbons

K_2PtCl_4 in aqueous medium is often used for the selective oxidation of isolated C-H bonds of saturated hydrocarbons. Ethane can be selectively oxidized to acetic or glycolic acid. Tetrahydrofuran is oxidized to γ-butyrolactone (eq 1), and isovaleric acid to γ-valerolactone (eq 2).



(1)



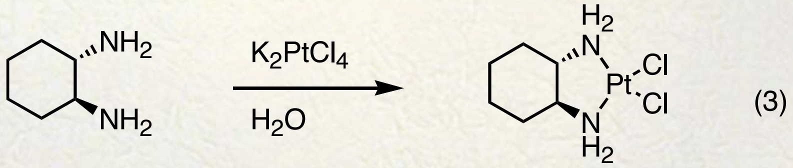
(2)

3.6:1

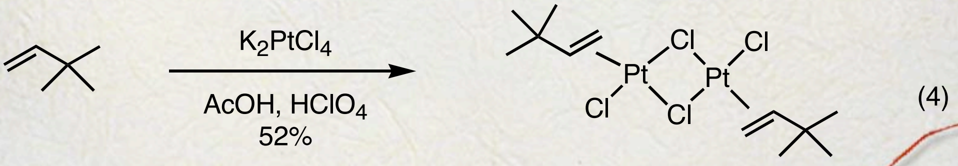
Dipotassium Tetrachloroplatinate(II), K_2PtCl_4

Starting material for the Synthesis of Pt-Complexes

The reaction of 1,2-diamines and similar ligands with K_2PtCl_4 is widely used for the synthesis of cisplatin analogs, powerful antitumor agents (eq 3).



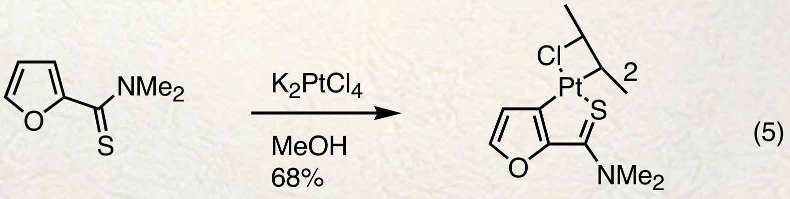
Alkenes, including ethylene, and dienes, readily coordinate with K_2PtCl_4, forming complexes (eq 4). These complexes readily undergo displacement reactions with free alkene in solution.



Dipotassium Tetrachloroplatinate(II), K_2PtCl_4

Starting material for the Synthesis of Pt-Complexes

A number of aromatic and heteroaromatic compounds, substituted with suitable donor ligands, undergo cycloplatination reactions when treated with K_2PtCl_4 (eq 5).

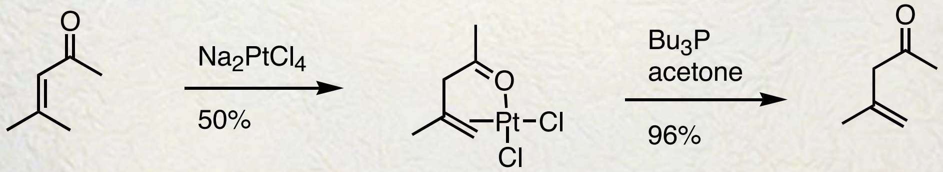


Disodium Tetrachloroplatinate(II), Na_2PtCl_4

Homogeneous hydrogen isotope exchange catalyst; selective oxidative functionalization of alkane C-H bonds; isomerization of alkenes.

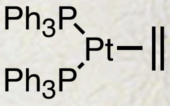
Alkene Isomerization

α,β–Unsaturated ketones can be isomerized to β,γ-unsaturated ketones through the formation of a π-complex with Na_2PtCl_4. Analogous reaction with Na_2PdCl_4 gives a stable π-allyl complex.



(3)

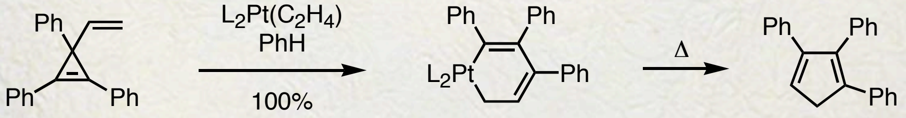
Ethylenebis(triphenylphosphine)platinum (0)



This is a nucleophilic metal species that readily undergoes ligand exchange with alkenes and alkynes; it acts as an efficient hydrosilation catalyst; oxidatively adds to activated C-X bonds and some C-C bonds, enabling rearrangement to occur.

Complexation with Alkenes

The title reagent readily undergoes alkene ligand exchange, possibly via the unsaturated L_2Pt ($L=Ph_3P$) as the active species. Numerous platinum alkene complexes have been synthesized by this procedure. Electron-deficient multiple bonds are generally more strongly bound, leading to more stable complexes. In some instances, alkene complexation is a preliminary to rearrangement of the carbon framework via the intermediacy of a σ bound organo platinum species (eqs 1 and 2).



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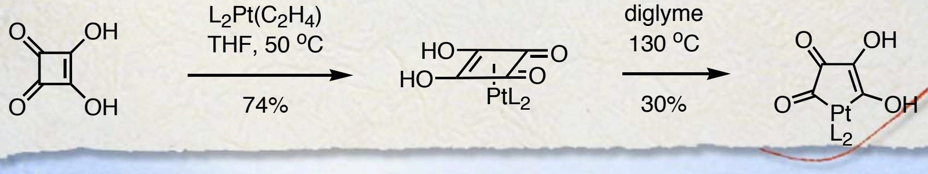

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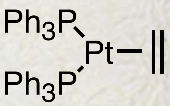
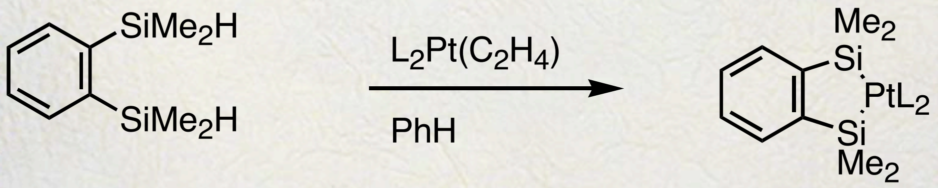
Ethylenebis(triphenylphosphine)platinum (0)



Hydrosilation

The title reagent has been used to catalyze hydrosilation of a variety of functional groups, typically employing 2-4 mol% of catalyst. Tanaka has used *o*-bis(dimethylsilyl)benzene to enable double silation of functional groups. The postulated intermediate formed from the catalyst and silane is a bis(silyl) platinum species (eq 3). Aldehydes and ketones have been shown to add silicon across the C=O bond, whereas unsaturated carbonyl compounds undergo 1,2- or a 1,4-addition depending on the steric environment (eq 4). Styrene reacts in a 1,1-fashion, presumably via a hydride shift, to afford the *gem*-disilyl derivative, whereas isoprene reacts in the more usual 1,2-mode (eq 5). More recently, silicon polymers have been prepared by employing tetrakis(dimethylsilyl)benzene and diynes (eq 6).



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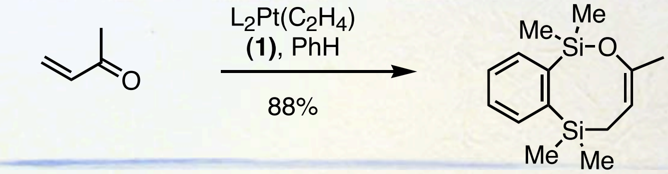

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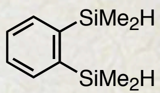

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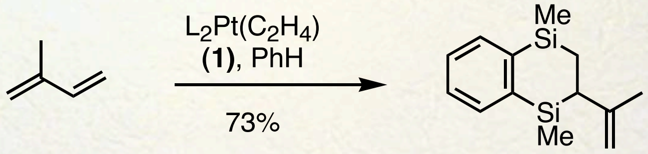

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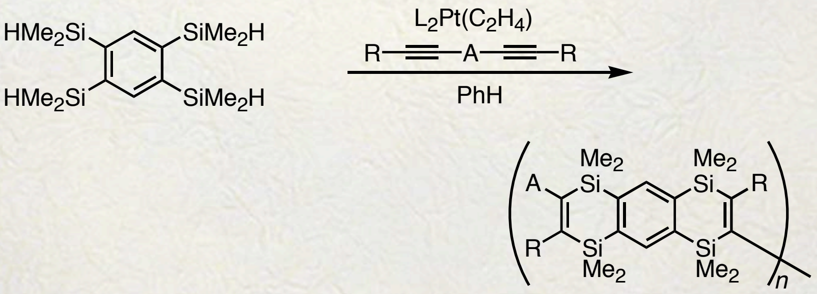
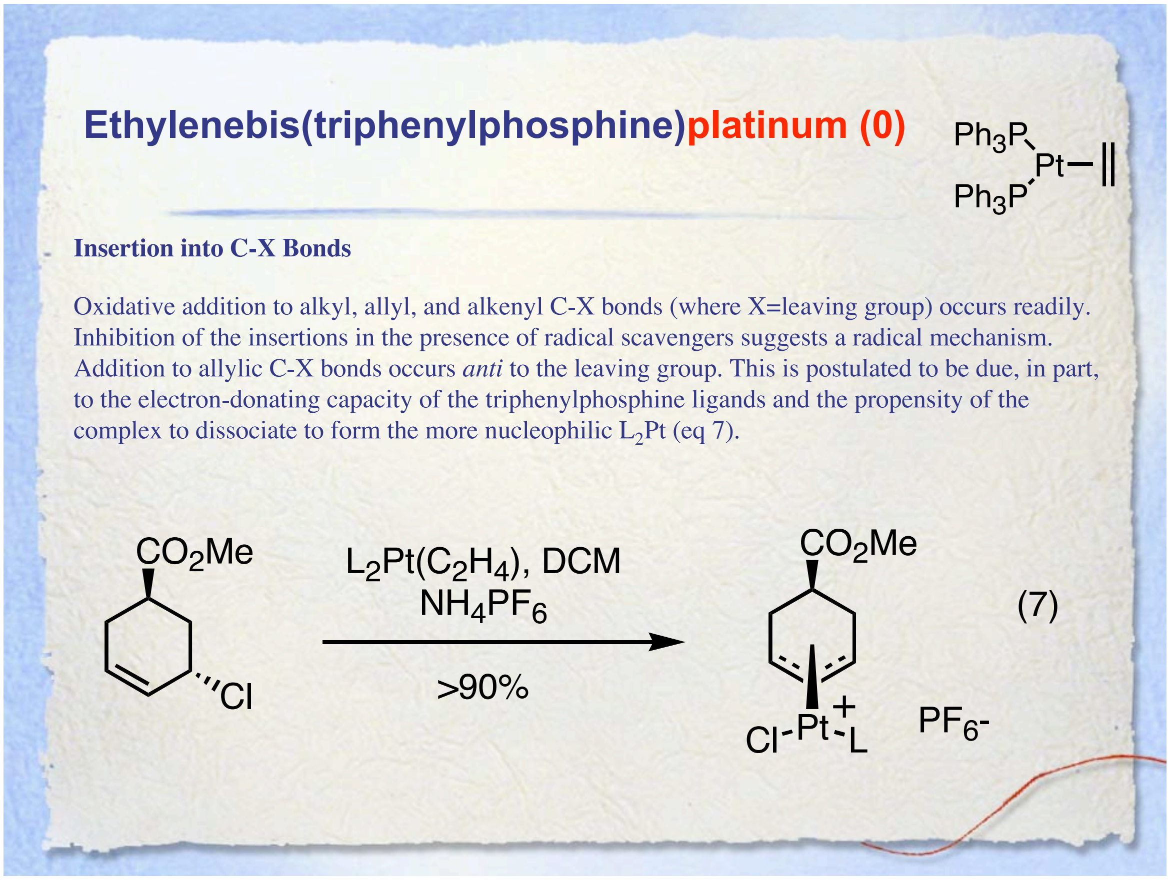


(6)

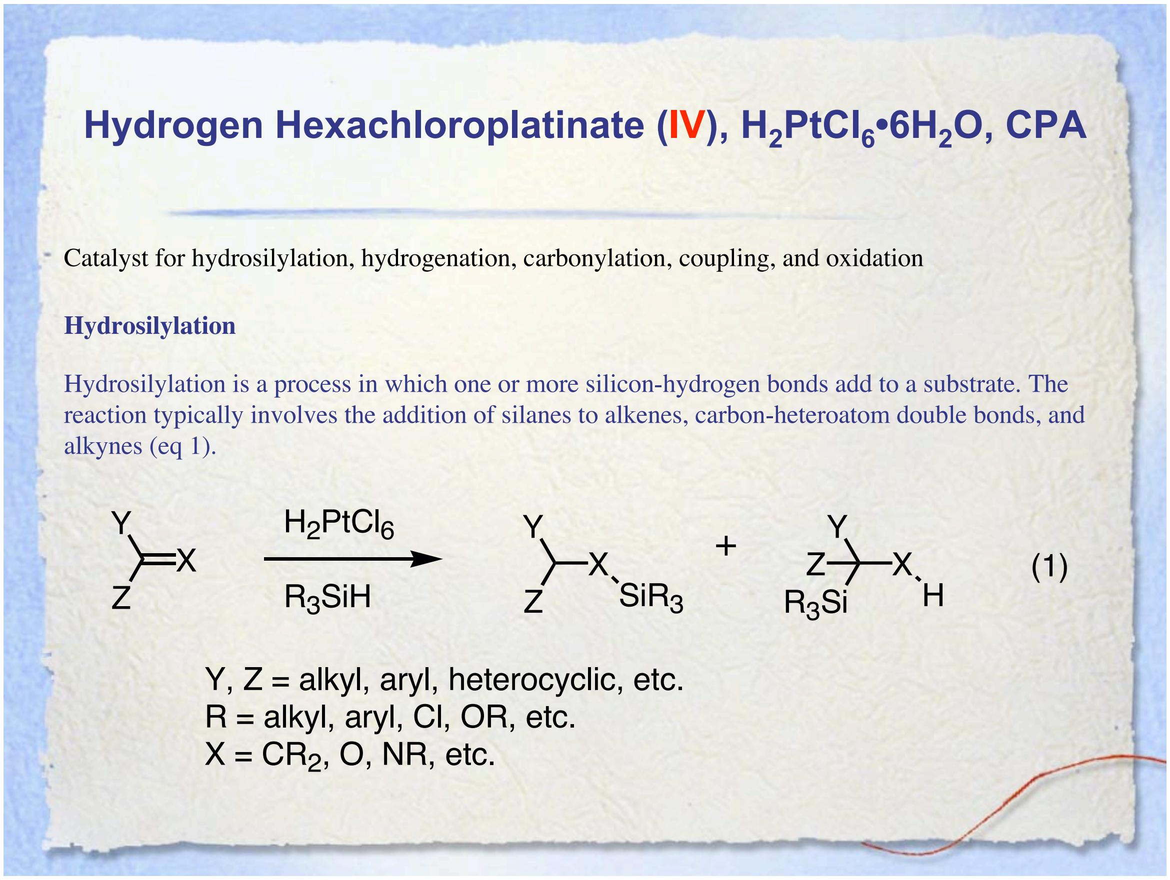
R = Hex, A = Ph, 78%
R = Ph, A = Fe(Cp)$_2$, 94%



Ethylenebis(triphenylphosphine)platinum (0)

Insertion into C-X Bonds

Oxidative addition to alkyl, allyl, and alkenyl C-X bonds (where X=leaving group) occurs readily. Inhibition of the insertions in the presence of radical scavengers suggests a radical mechanism. Addition to allylic C-X bonds occurs *anti* to the leaving group. This is postulated to be due, in part, to the electron-donating capacity of the triphenylphosphine ligands and the propensity of the complex to dissociate to form the more nucleophilic L_2Pt (eq 7).



Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6 \cdot 6H_2O$, CPA

Catalyst for hydrosilylation, hydrogenation, carbonylation, coupling, and oxidation

Hydrosilylation

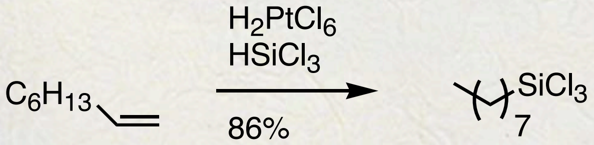
Hydrosilylation is a process in which one or more silicon-hydrogen bonds add to a substrate. The reaction typically involves the addition of silanes to alkenes, carbon-heteroatom double bonds, and alkynes (eq 1).

Y, Z = alkyl, aryl, heterocyclic, etc.
R = alkyl, aryl, Cl, OR, etc.
X = CR_2, O, NR, etc.

Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6 \cdot 6H_2O$, CPA

Hydrosilylation

A dilute solution of this complex in isopropanol is typically used as the catalyst (**Speier's** catalyst). CPA also serves as the starting material for a very active form of homogeneous platinum (0) catalyst known as the **Karstedt** catalyst. The major features of hydrosilylations are: an induction period; moderate to good yields; facility of the reaction on the nature of the silane, substrate, and the catalytic species; isomerization of the alkene substrate; and applications to a wide variety of substrates. A generally accepted mechanism for hydrosilylation has been proposed by Chalk and Harrod. It involves the coordination of the metal to the alkene followed by oxidative addition of the silane to the metal to give a Pt(IV) intermediate. Rearrangement gives σ-bonded Pt(IV) and subsequent reductive elimination gives the hydrosilylated product and Pt(II) species. Hydrosilylation reactions of electron-rich alkenes with activated silanes such as halo- or alkoxysilanes are simple. Terminal alkenes react with trichlorosilane under CPA catalysis to furnish high yields of the linear trihalosilane (eq 2).

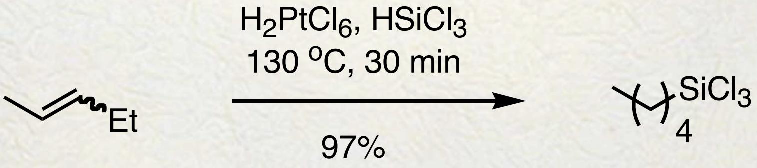


(2)

Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6 \cdot 6H_2O$, CPA

Hydrosilylation

Hydrosilylations of internal alkenes with trichlorosilane and CPA as the catalyst proceed in a different manner. In these reactions, both bond migration and hydrosilylation occur. For example, reaction of 2-pentene with trichlorosilane for 30 min at 130 °C using CPA as the catalyst furnishes the terminal silane (eq 3).



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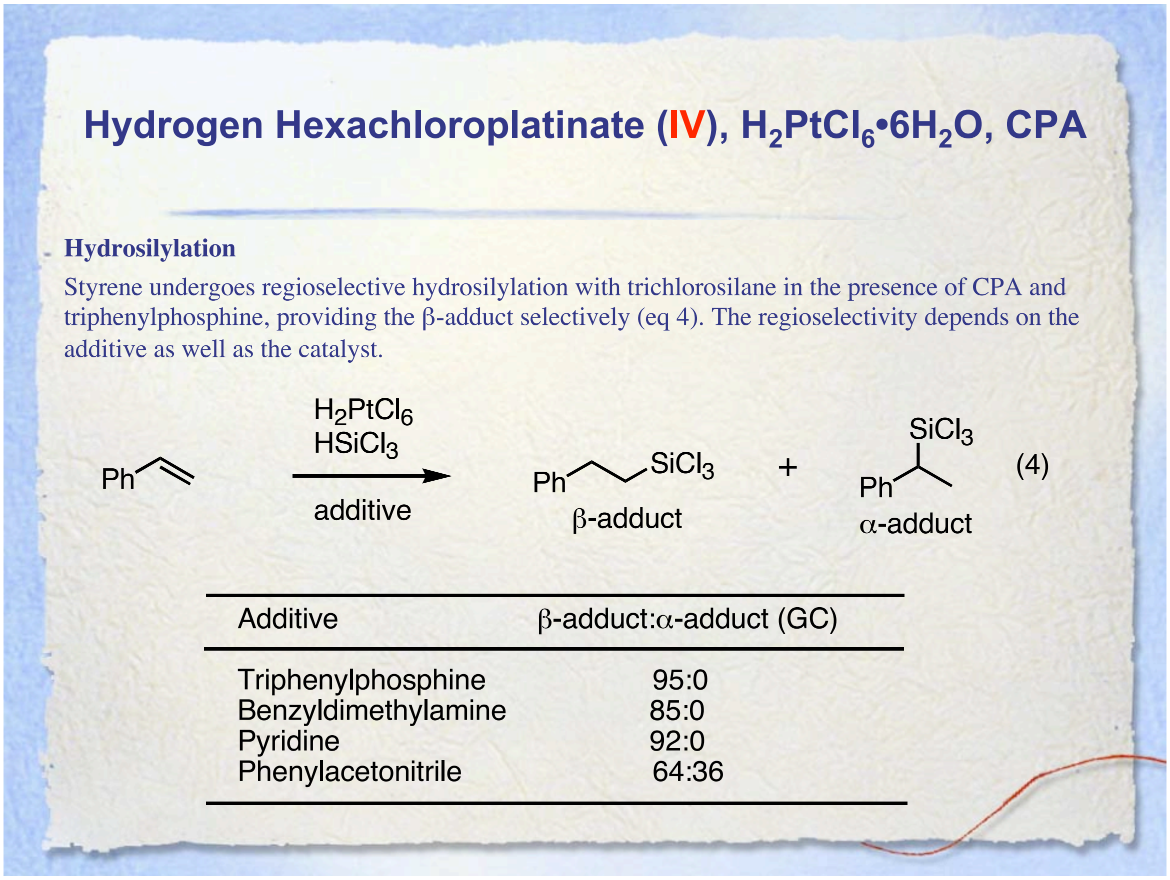
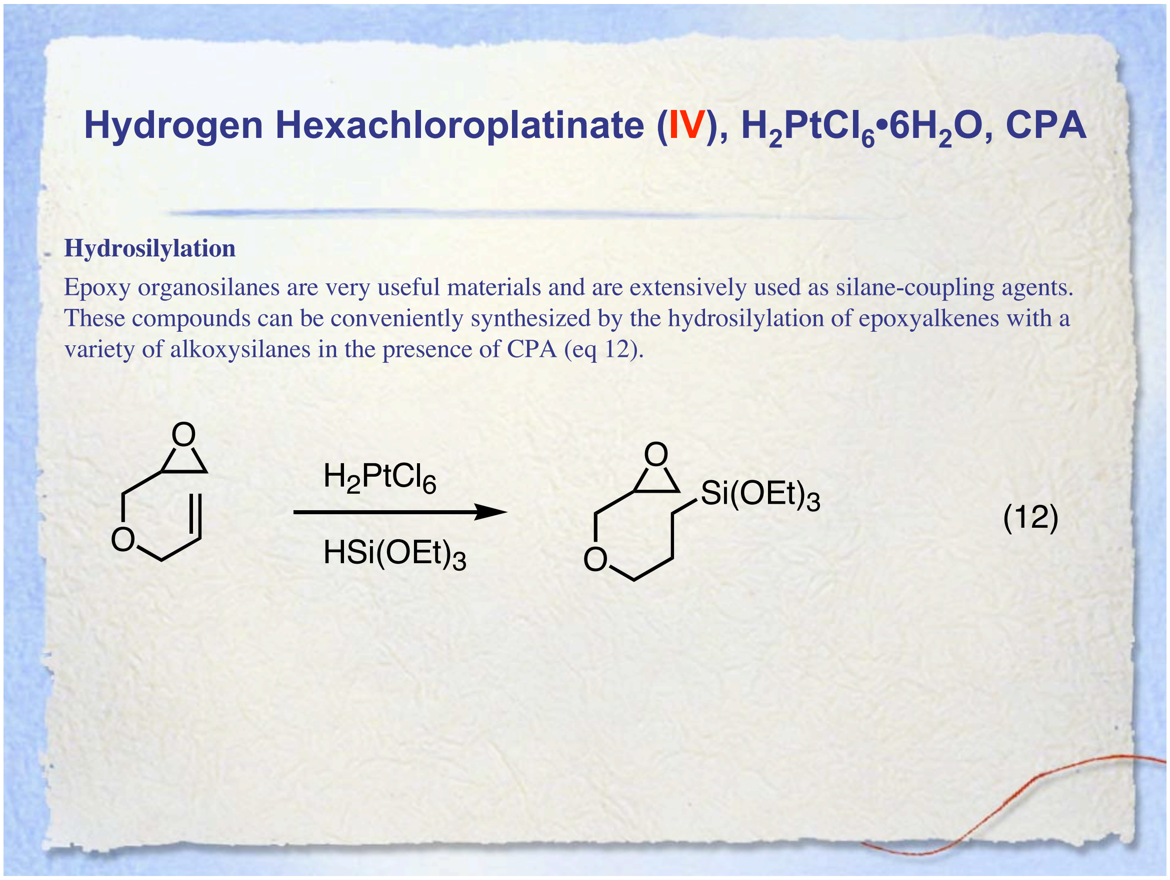


Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6{\bullet}6H_2O$, CPA

Hydrosilylation

Styrene undergoes regioselective hydrosilylation with trichlorosilane in the presence of CPA and triphenylphosphine, providing the β-adduct selectively (eq 4). The regioselectivity depends on the additive as well as the catalyst.

Additive	β-adduct:α-adduct (GC)
Triphenylphosphine	95:0
Benzyldimethylamine	85:0
Pyridine	92:0
Phenylacetonitrile	64:36



Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6{\bullet}6H_2O$, CPA

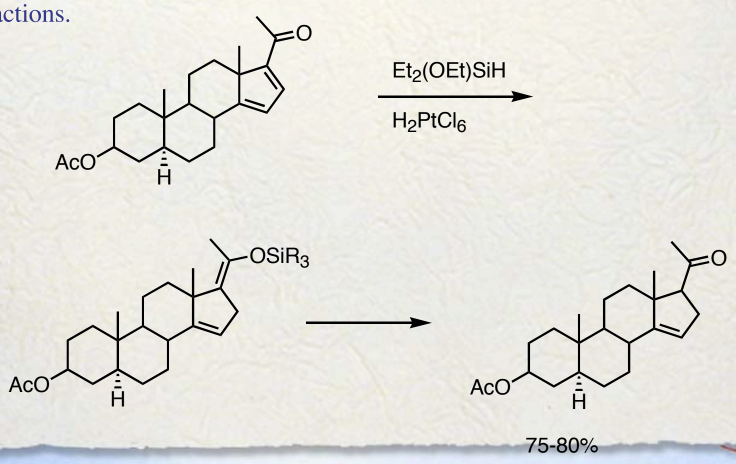
Hydrosilylation

Epoxy organosilanes are very useful materials and are extensively used as silane-coupling agents. These compounds can be conveniently synthesized by the hydrosilylation of epoxyalkenes with a variety of alkoxysilanes in the presence of CPA (eq 12).

Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6\cdot 6H_2O$, CPA

Hydrosilylation

Hydrosilylation of enones proceeds by a 1,4-addition of the silane to produce the enol silyl ethers, from which the reduced compounds are obtained through hydrolysis. An application of this methodology is illustrated in the synthesis of a precursor to purpnigenin (eq 29). Of the many silanes examined in this reaction, diethylethoxysilane gave the highest yields and least number of side reactions.



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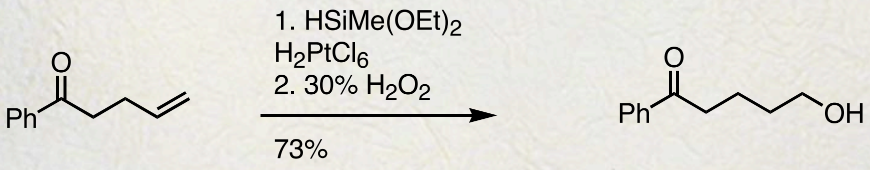
Hydrogen Hexachloroplatinate (IV), $H_2PtCl_6\cdot 6H_2O$, CPA

Hydrosilylation followed by Oxidation

Tamao and co-workers have developed elegant methodologies for the conversion of the silyl intermediates obtained in hydrosilylation of alkenes and alkynes to a variety of functional groups. The key transformations in these methodologies include the oxidation of a C-Si bond to a hydroxy group with retention of configuration, the conversion of a C-Si bond to a C-Br bond, and conversion of a C-Si bond to a C-C bond. The hydrosilylation-oxidation sequence can be effectively used for the transformations of terminal alkenes to the corresponding anti-Markovnikov alcohols (eq 30). The silane used in these experiments, methyldiethoxysilane, is commercially available and air stable. Thus the hydrosilylations can be carried out without solvent under air using CPA catalysis. Hydrogen peroxide oxidation proceeds smoothly only if there is at least one alkoxy group on the silicon. The reactivity of the carbon attached to silicon can be controlled by the nature of the alkoxy group.



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