Synthesis of Pd Nanoparticles Supported Pd(II) Complexes and Catalytic Olefin Hydrogenation and Isomerization Reactions

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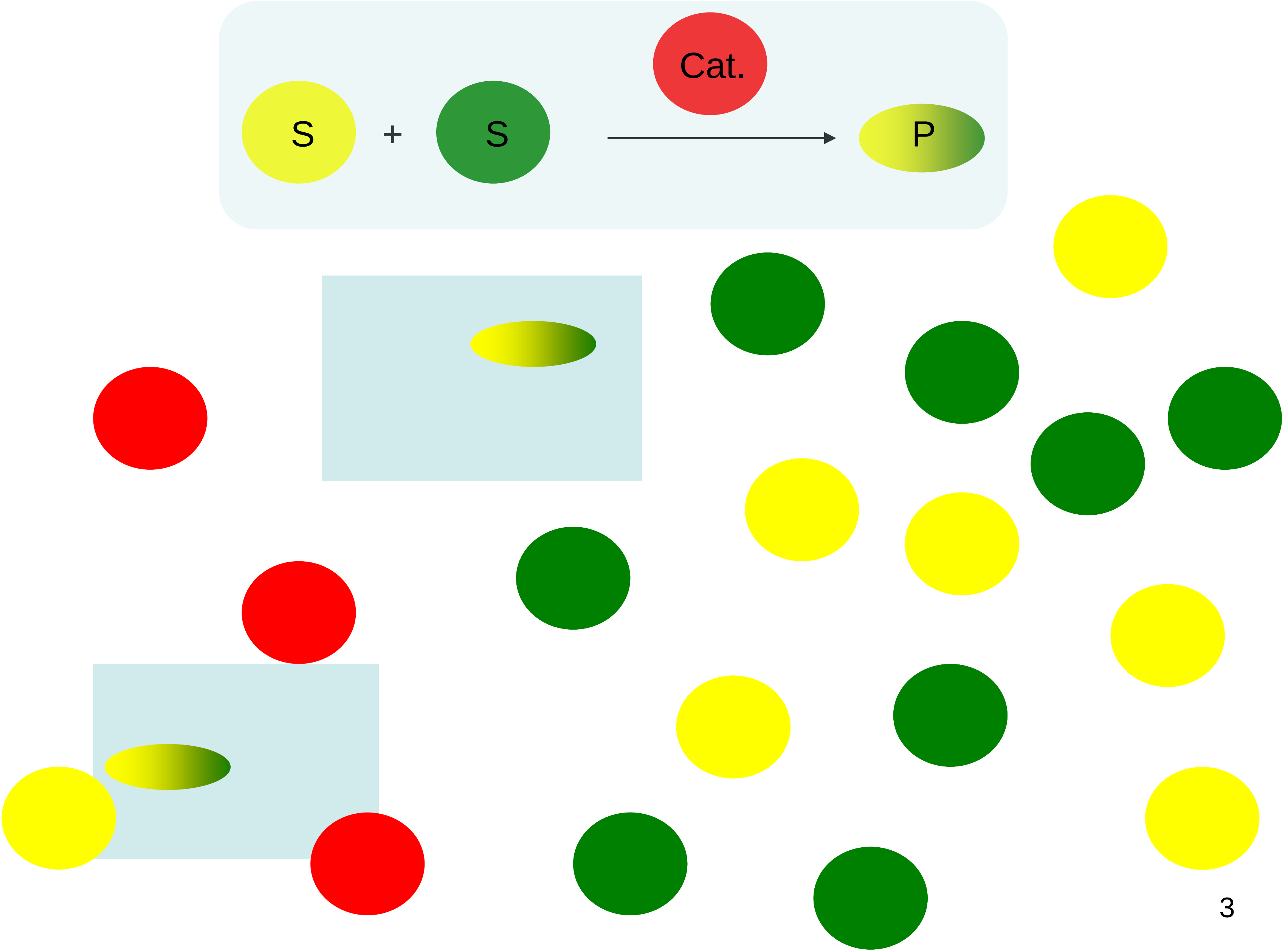
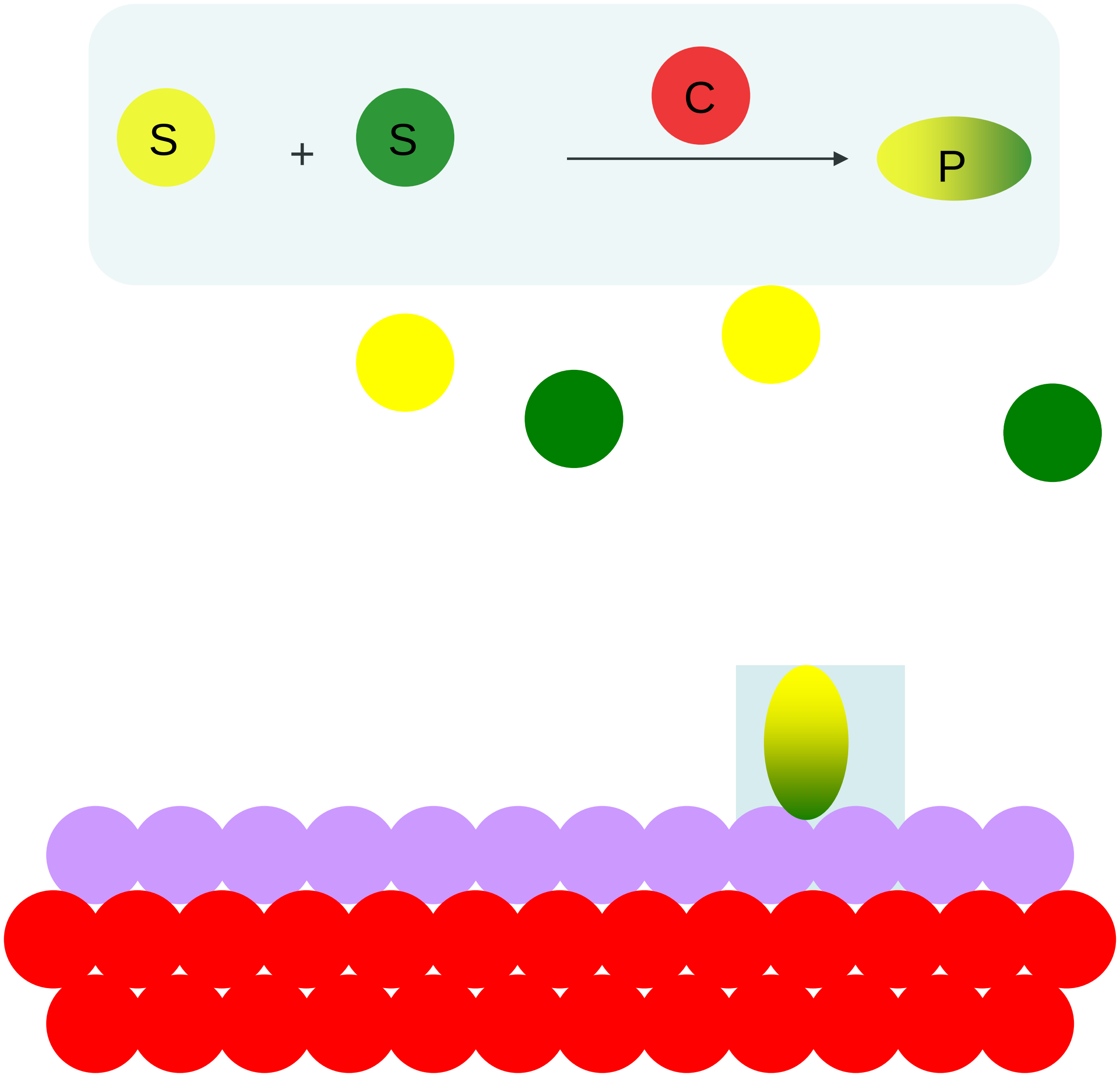
Types of Catalysts

Characteristics of catalysts	Homogenous	Heterogeneous	Hybrid
Cat. structure	Known	Unknown	Known
Catalyst modification	Easy	Difficult	Easy
Activity	High	Low	High
Selectivity	High	Low	High
Poisoning of cat.	High risk	Low risk	Low risk
Mechanical strength	Low	High	High
Cat. stabilities	Low	High	High
Conditions of catalysis	Mild	Harsh	Mild
Separation & recycle of cat.	Difficult	Easy	Easy
Industrialization	Difficult	Accessible	Accessible

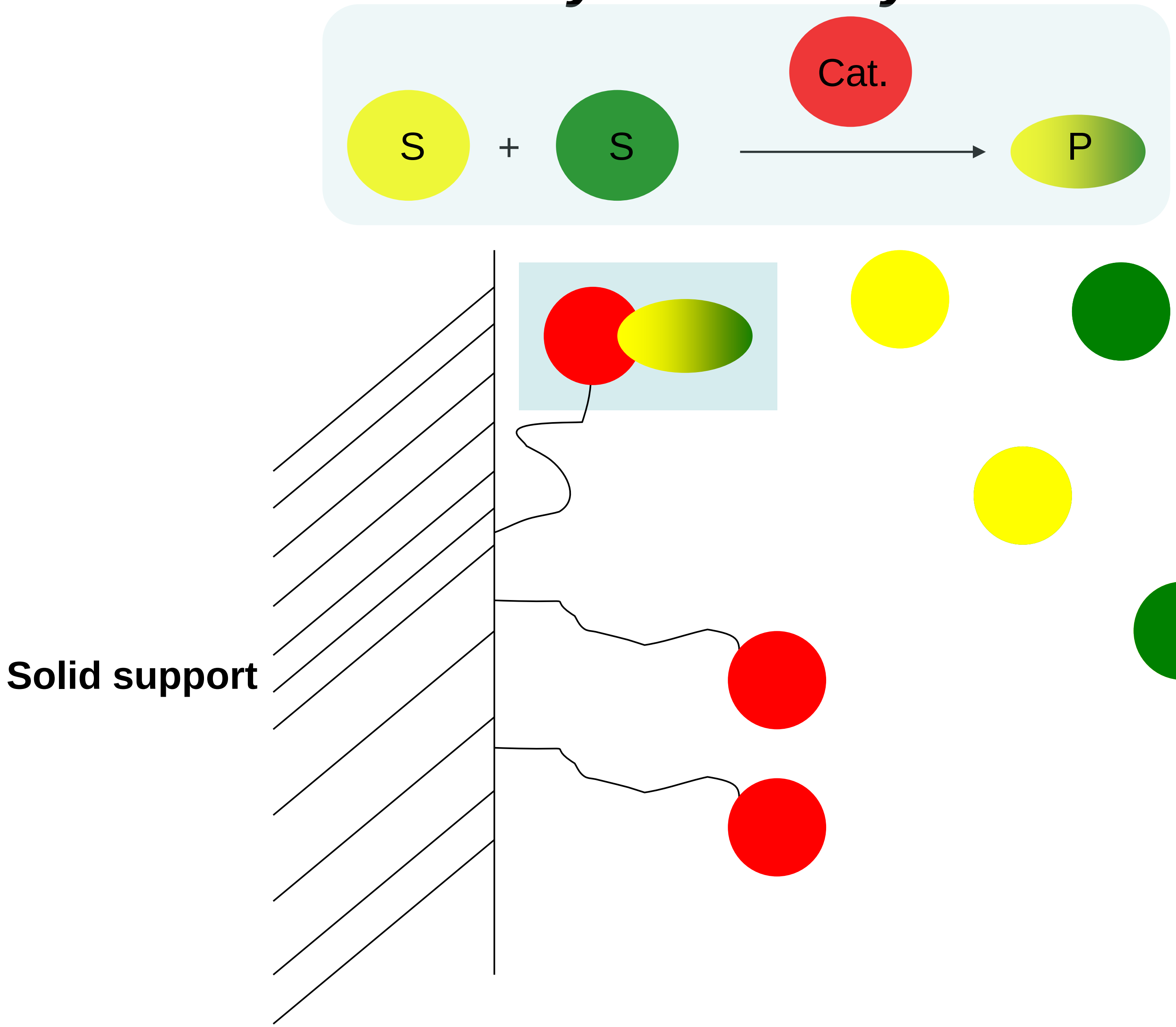
Homogeneous Catalyst



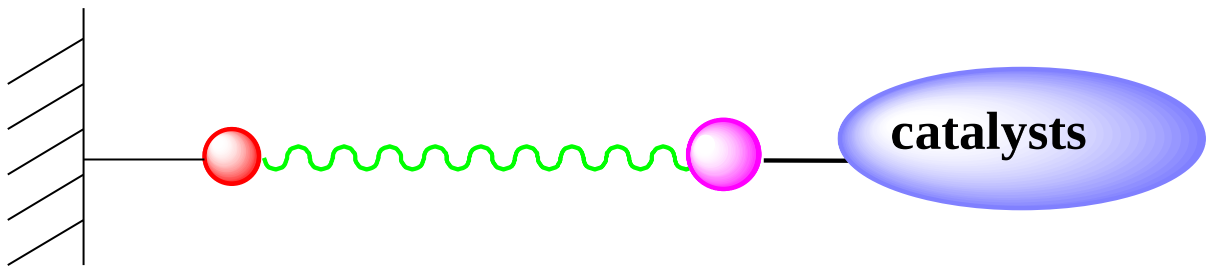
Heterogeneous Catalyst



Hybrid Catalyst



The Componemts of Hybrid Catalyst



Metal oxide
Organicpolymer
Silica gel

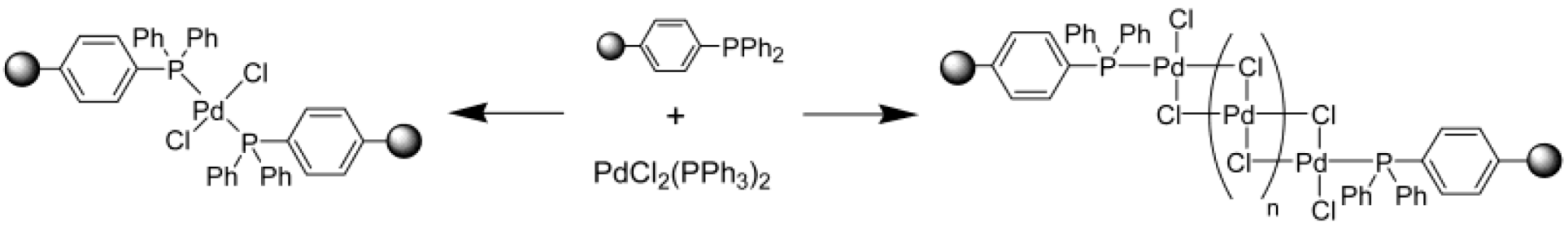
Soluble metal complex

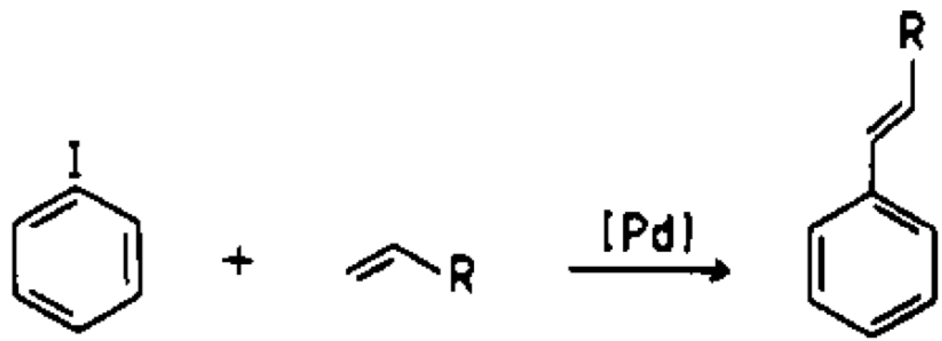
functional groups

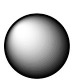
coordination ligands

spacer linker

Phosphines Attached to Polymer-Supported Peptides

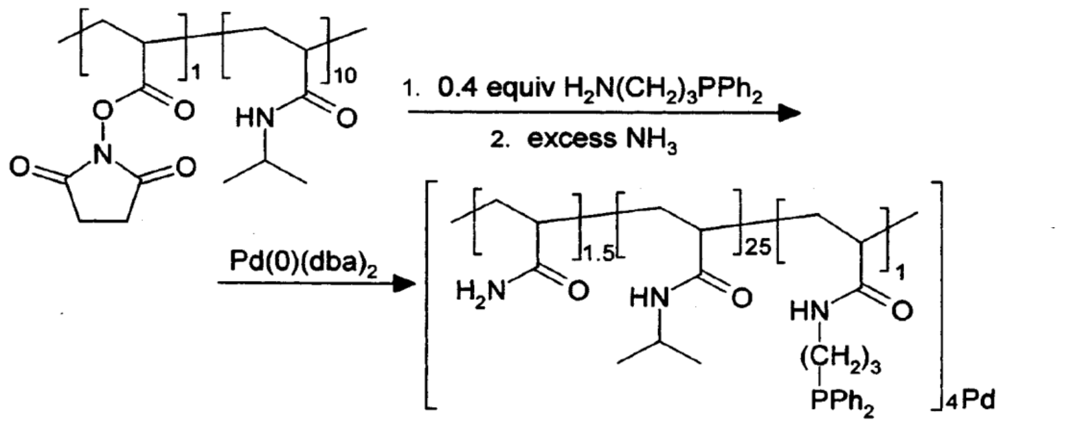


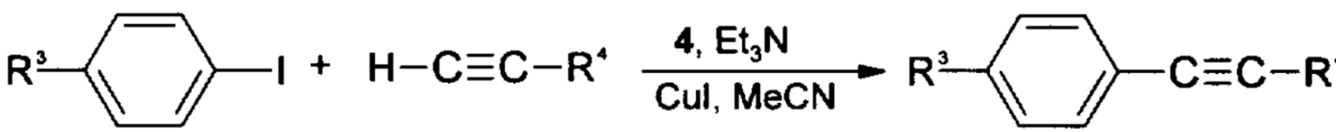


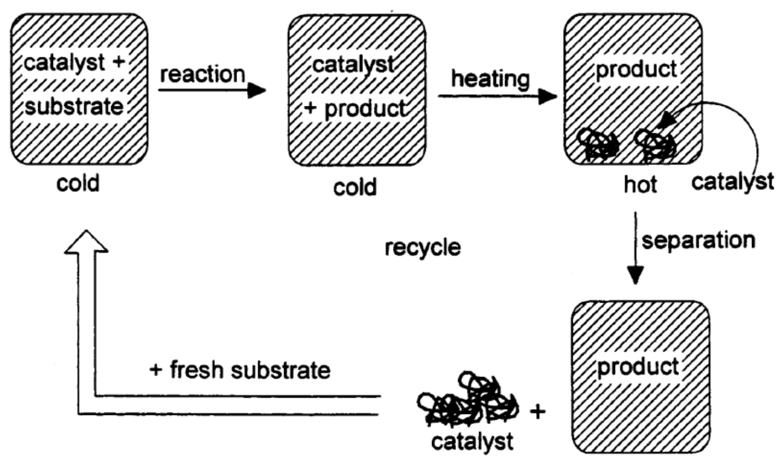
 : polystyrene

Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217-3274

Solid/Liquid Separations of Catalysts on Polymers



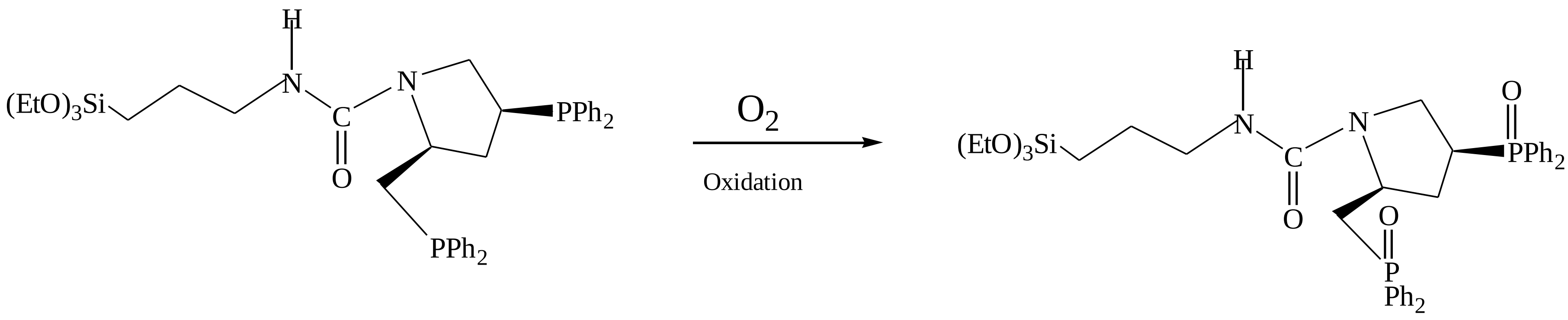




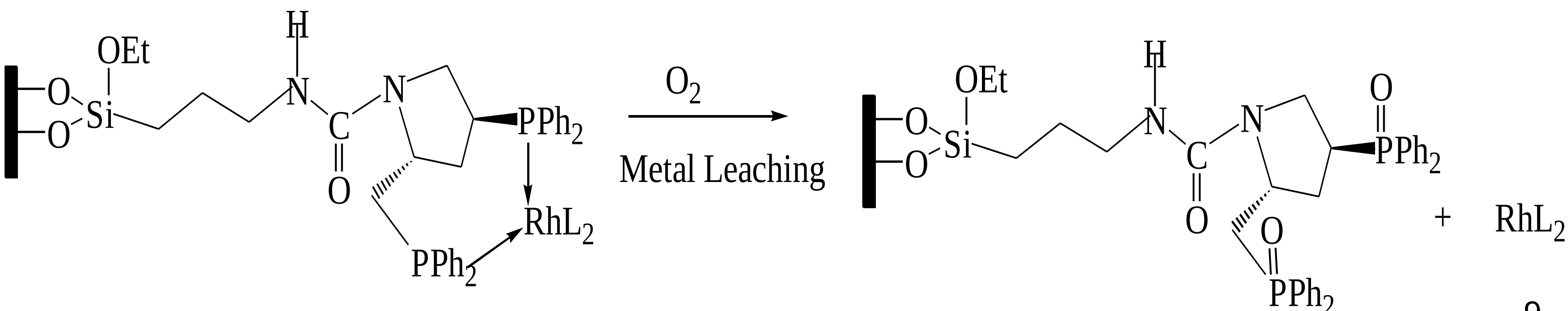
Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345-3384.

The Limitation of Phosphine Ligand

a. Oxidation

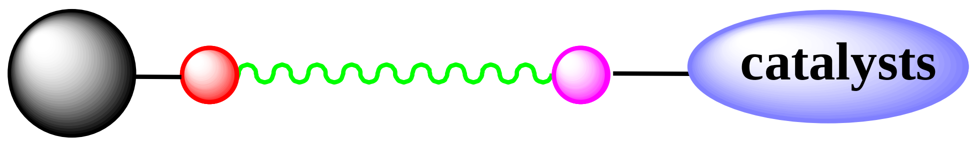


b. Metal Leaching



Kinzel, E. *J. Chem. Soc. Chem. Commun.* **1986** 1098

Catalyst Design



Nanoparticles

with controllable solubility

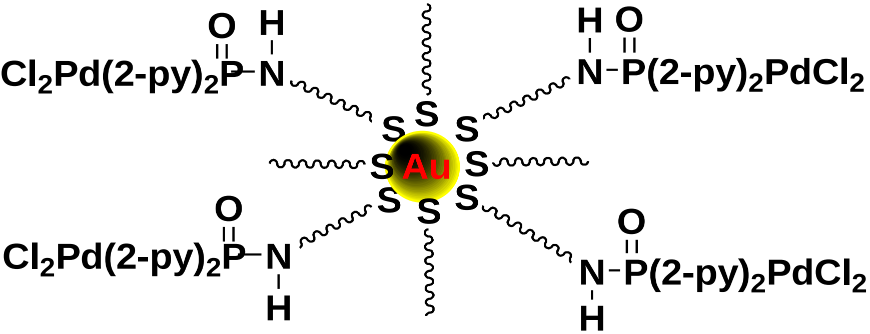
Soluble metal complex

functional groups

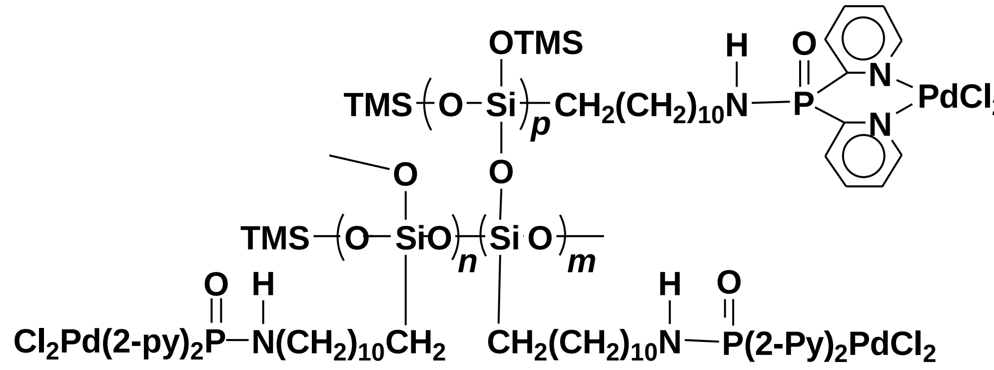
coordination ligands

spacer linker

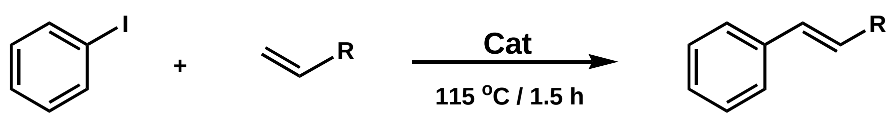
Gold NPs-Supported and SiO_2-Supported Catalysts



Au-HS$(CH_2)_{11}$N(H)(O)P(2-py)$_2$PdCl_2 (Au-L-Pd)



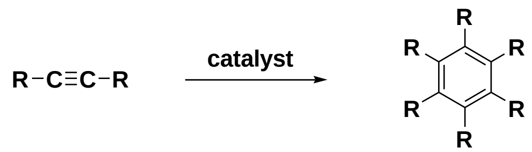
SiO_2-L-Pd



	TOF (h^{-1})				
	R				
Cat.	**COOMe**	**COOEt**	**COO^{n}Bu**	**COO^{t}Bu**	**Ph**
Pd(MeCN)$_2$Cl$_2$	**11100**	**15020**	**14500**	**13150**	**4250**
Au-L-Pd[a]	**47333**	**48667**	**45333**	**44667**	**18667**
SiO_2-L-Pd	**9000**	**10000**	**7111**	**9666**	**4366**

[a]Pd/S$(CH_2)_7CH_3$ = 1:1.4 (mole ratio)

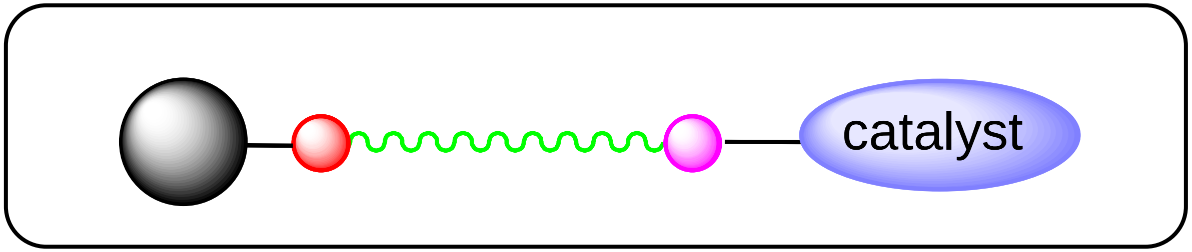
Catalytic [2+2+2] Alkyne Cyclotrimerization Reactions



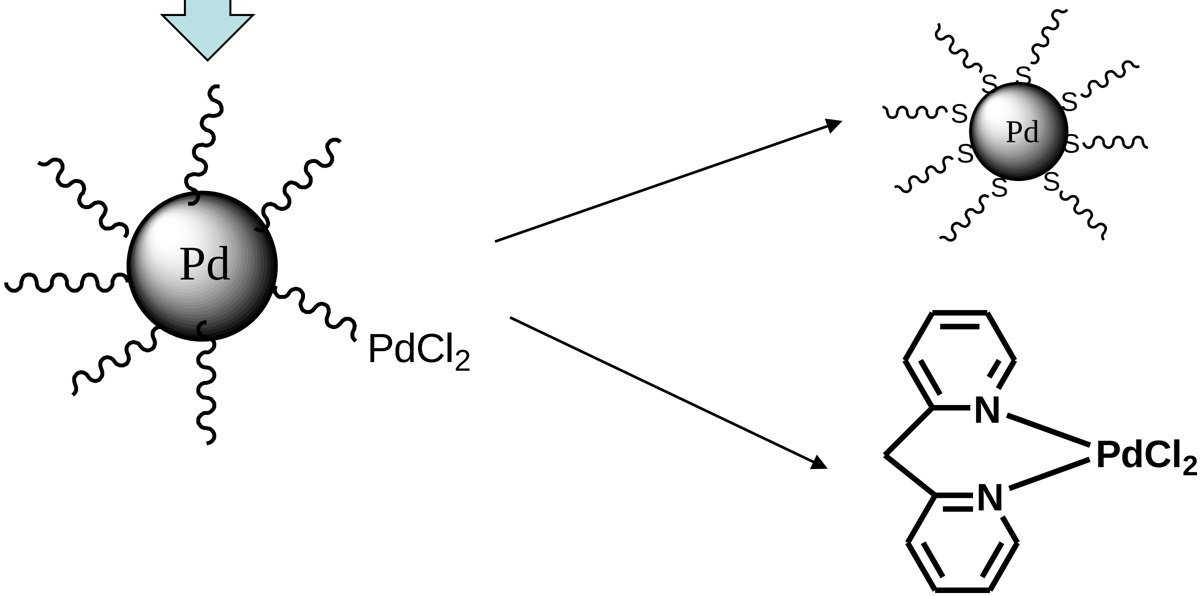
Alkyne R	*catalyst*	*solvent*	*T* (^{o}C)	*time* (min)	*conversion*[c] (%)
^{n}Pr	Au-L-Pd $Pd(CH_3CN)_2Cl_2$	$CDCl_3$	rt	40	99 53
Et	SiO_2-$PdCl_2$ [b] Au-L-Pd	$CDCl_3$	rt	30	6 99

[a]Reaction conditions: alkyne (0.075 mmol) in $CDCl_3$ (1 mL), catalyst loading = 4 mol%. [b]alkyne (0.56 mmol) in $CDCl_3$ (3 mL), catalyst loading = 4 mol%.. [c]Conversions were determined by ^{1}H-NMR spectroscop [d]Products were purified and isolated by flash chromatography on SiO_2 with hexane/ethyl acetate. [e]Isomers ratios were determined by GC.

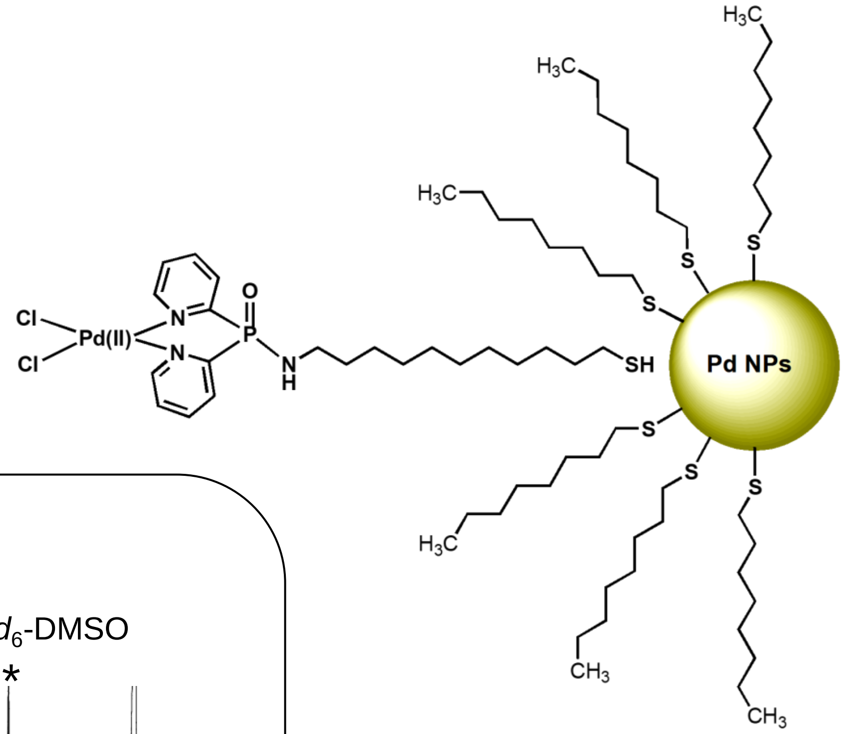
Motivation and Design



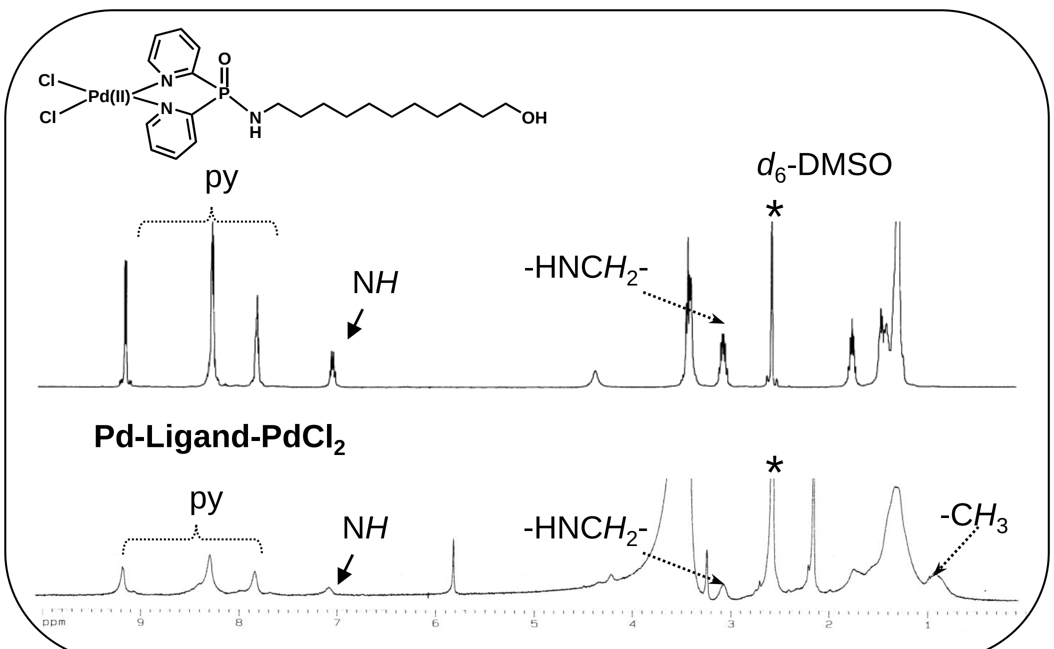
Alternative supporting materials



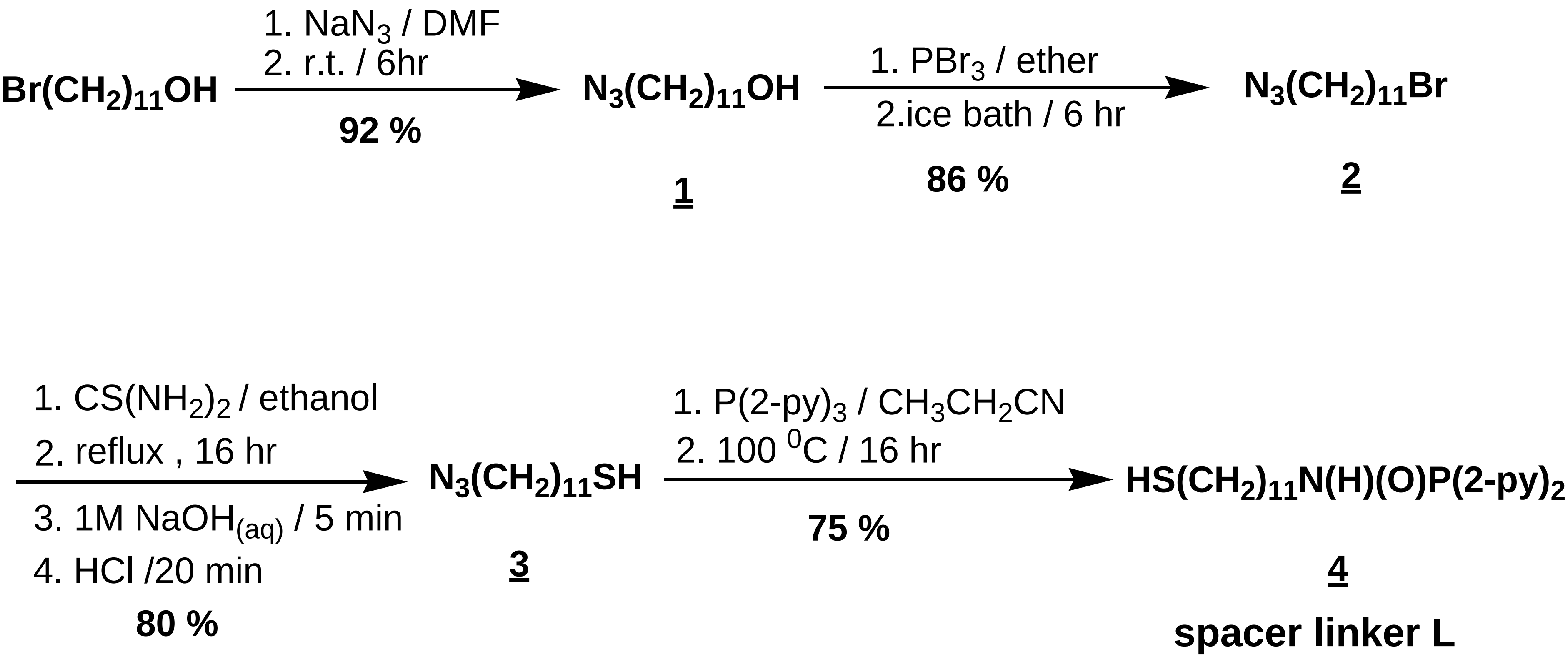
Palladium(II) Catalyst immobilized on Pd NPs



Pd-Ligand-PdCl$_2$



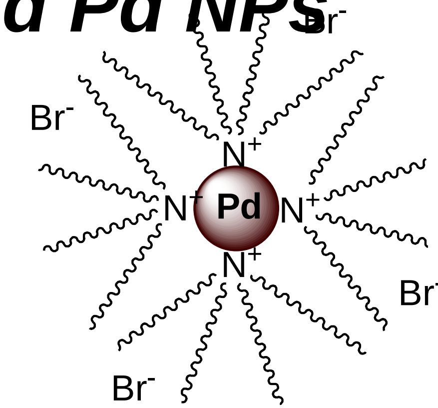
Synthesis of Spacer Linker



Bi-phase Synthesis of Octanethiol Protected Pd NPs

$PdCl_2(CH_3CN)_2$

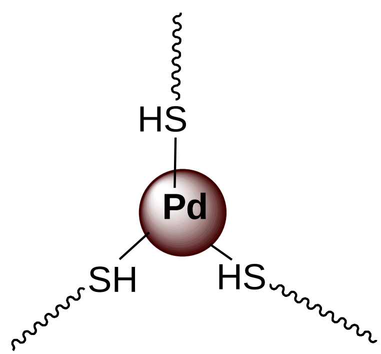
1. surfactant $[CH_3(CH_2)_7]_4N^+Br^-$ / $CHCl_3$
2. Sodium citrate / H_2O
3. reflux for 1 day



Pd-TOAB

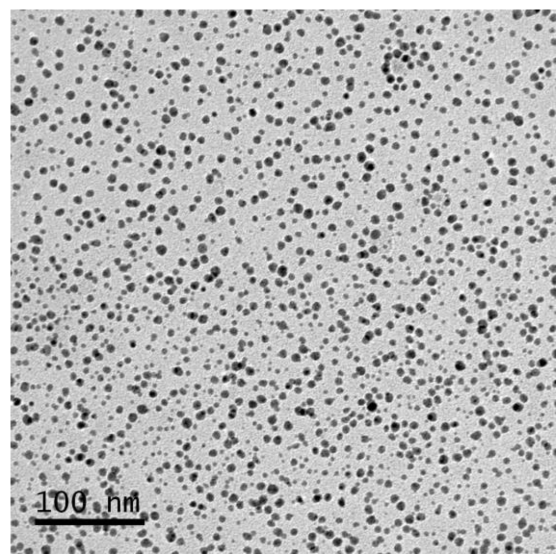
n-octanethiol

r.t / stir for 1 hr



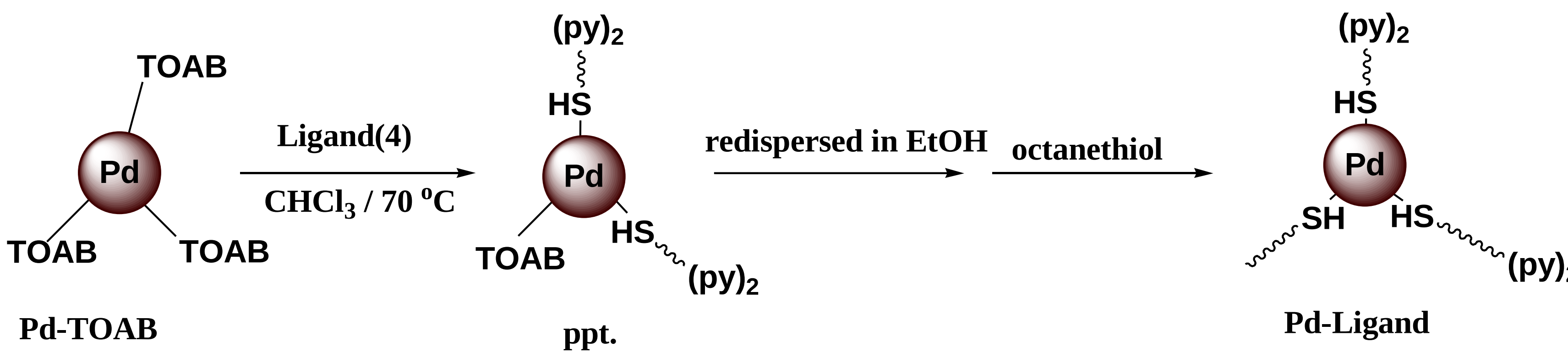
Pd-SR

40%

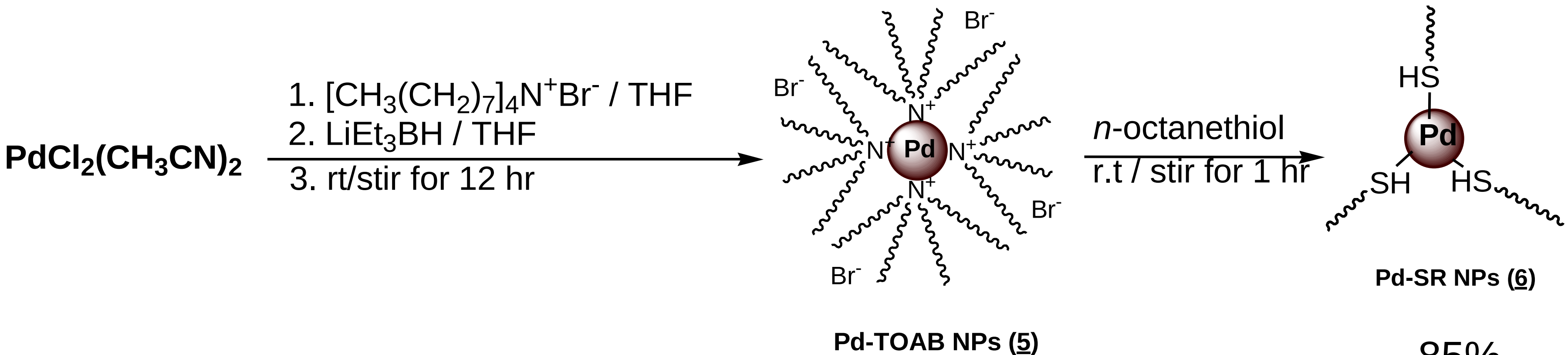


Particle size distribution = 4.52 ± 1.32 nm

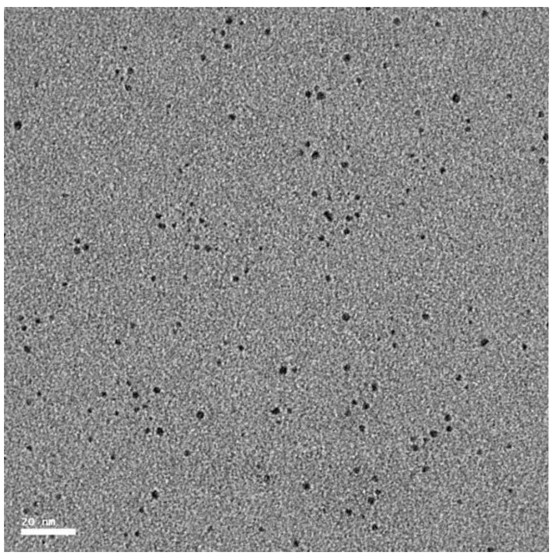
Synthesis of Pd-Immobilized Pd NPs

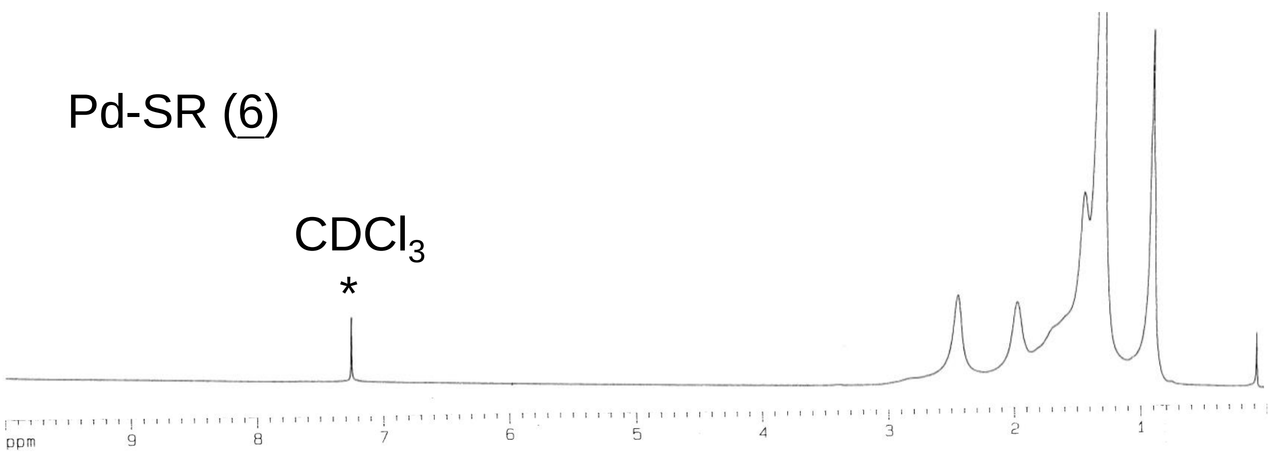


Single-phase Synthesis of Octanethiol Protected Pd-SR NPs (6)



85%

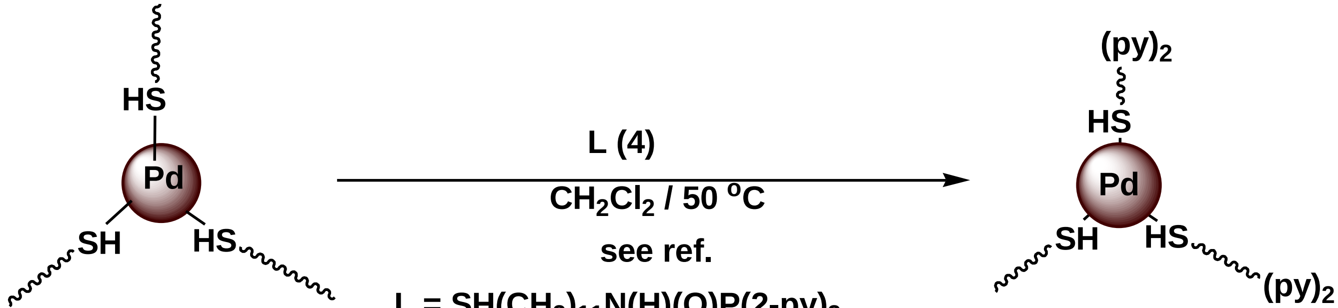




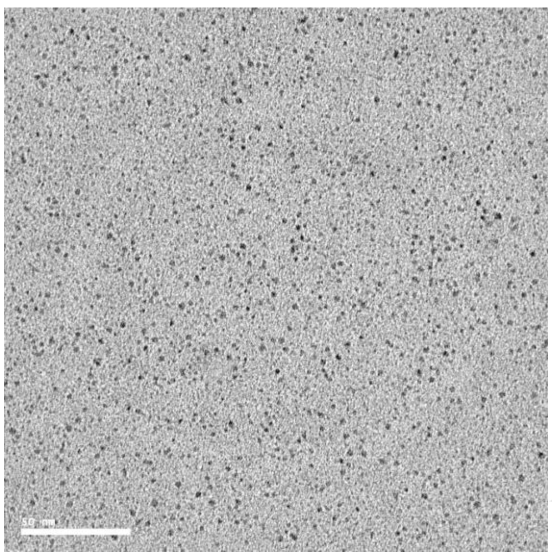
Particle size distribution = 2.60 ± 0.5 nm

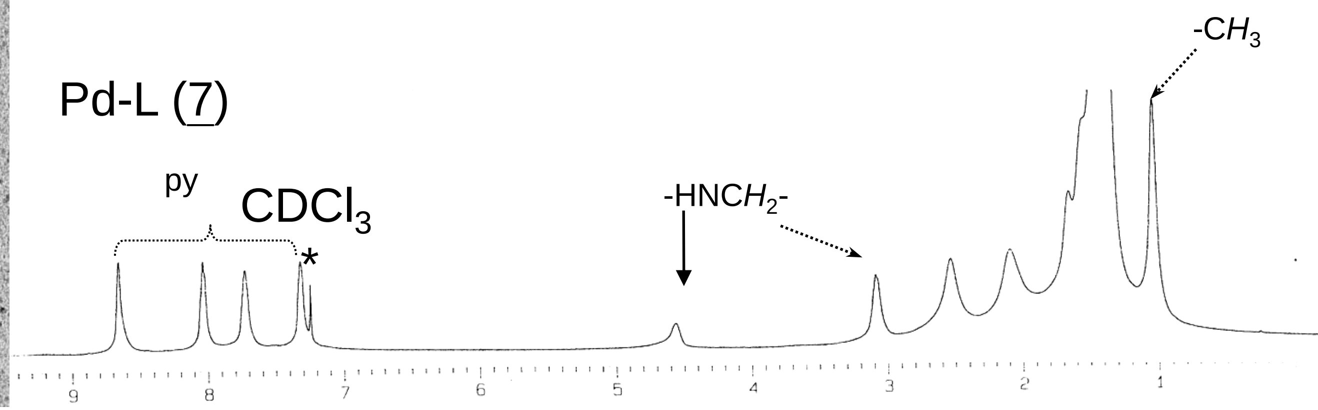
Langmuir **2002**, *18*, 1413-1418

Surface Functionalization of Pd-SR NPs



Pd-SR NPs (6) **Pd-L NPs (7)**

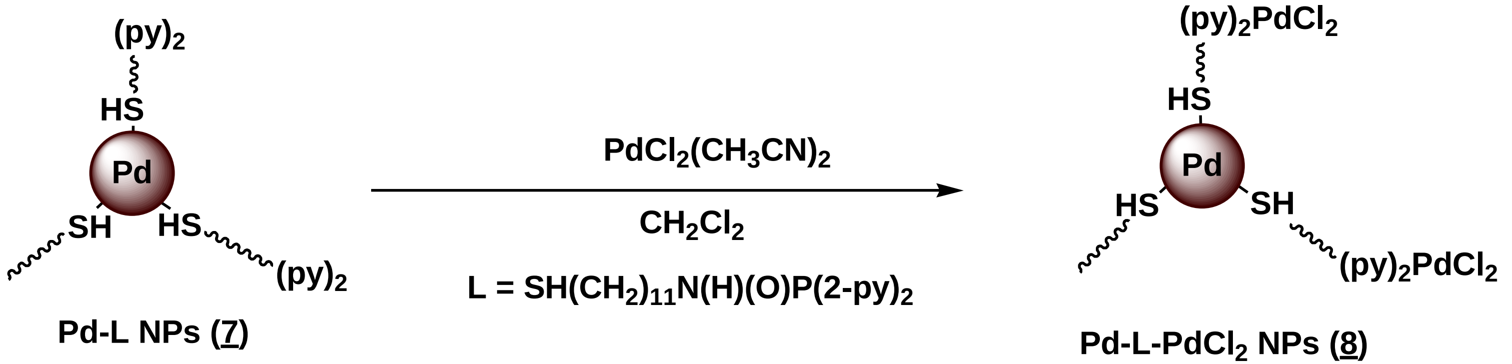


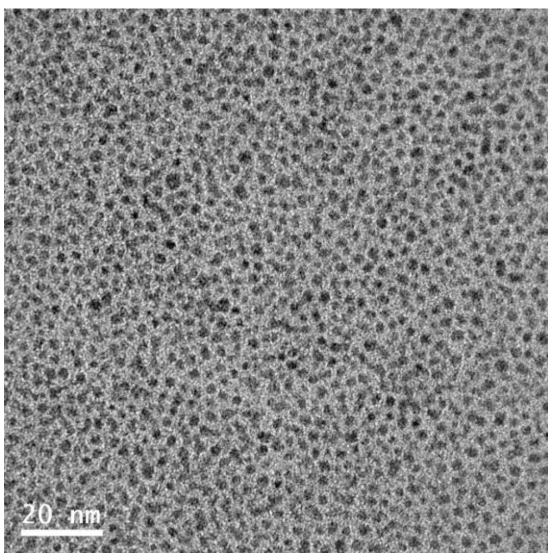


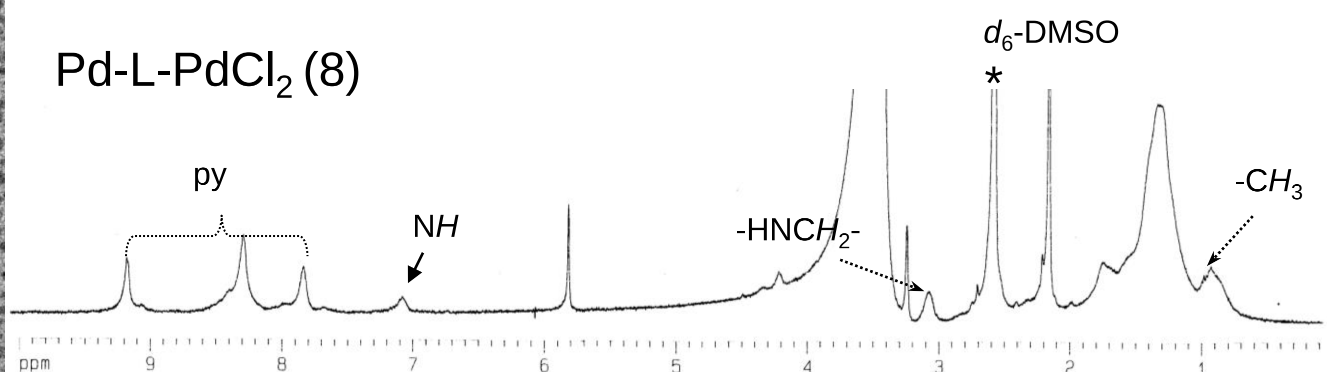
Particle size distribution
= 2.72 ± 0.5 nm

ref. : *Phys. Chem. Chem. Phys.* **2001**, *3*, 3377-3381

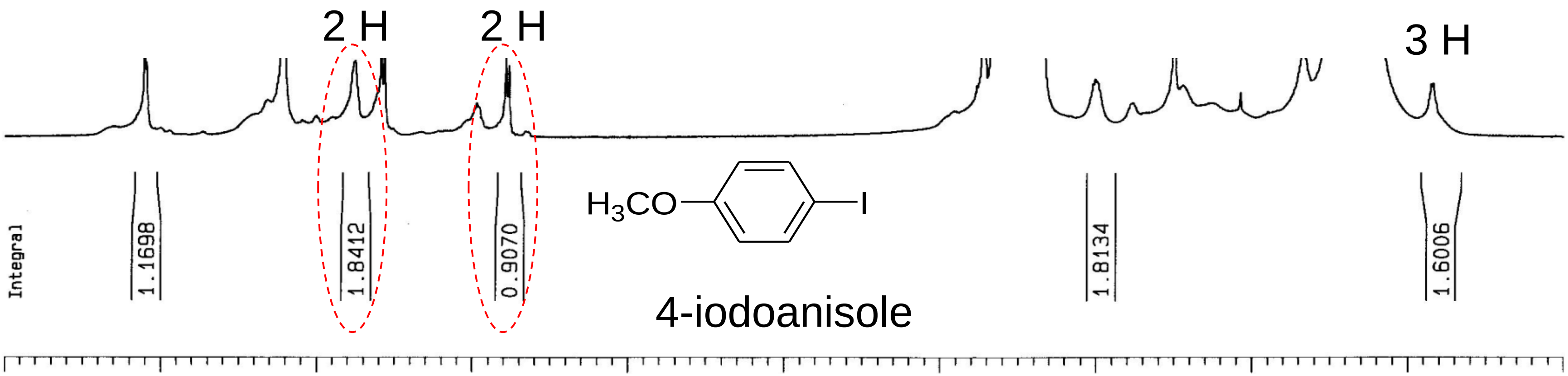
Immobilization of Soluble Pd(II) Complexes







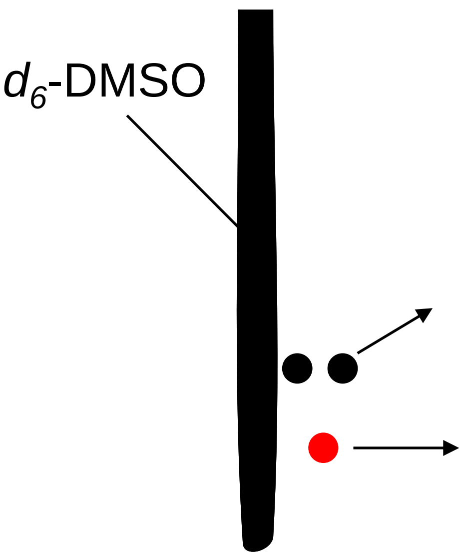
Particle size distribution
$= 2.41 \pm 0.5$ nm



Pd(II)-L :1.821×10^{-5} mol = 10.56 mg

thiol:1.214×10-5 mol = 1.77 mg

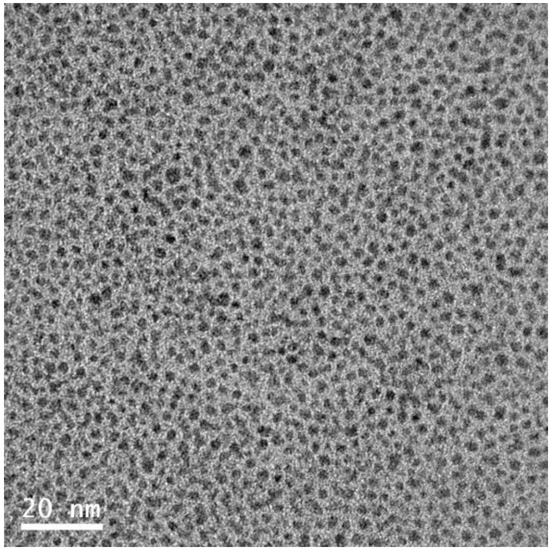
Pd NPs: 15.4-10.56-1.77= 3.07 mg



Pd-L-$PdCl_2$: 15.4 mg

4-iodoanisole: 2.1 mg

Calculation of Surface Pd NPs



Particle size distribution
= 2.41 ± 0.5 nm

單顆奈米原子團表面積：

代入 $r = r_0 \times n^{1/3}$

$1.2 = 0.169 \times n^{1/3} \rightarrow n = \underline{362}$ atom

$S = 4\pi\, r_0^2\, n^{2/3}$

$= 4\pi\, (169 \times 10^{-12})^2 \times 362^{2/3}$

$=1.82 \times 10^{-17}\ (m^2)$

單顆奈米原子團表面原子數：

$n_s = S / \pi\, r_0^2 = 1.82 \times 10^{-17} / \pi\, (169 \times 10^{-12})^2$

= 203 atom

表面原子數佔總原子數百分比

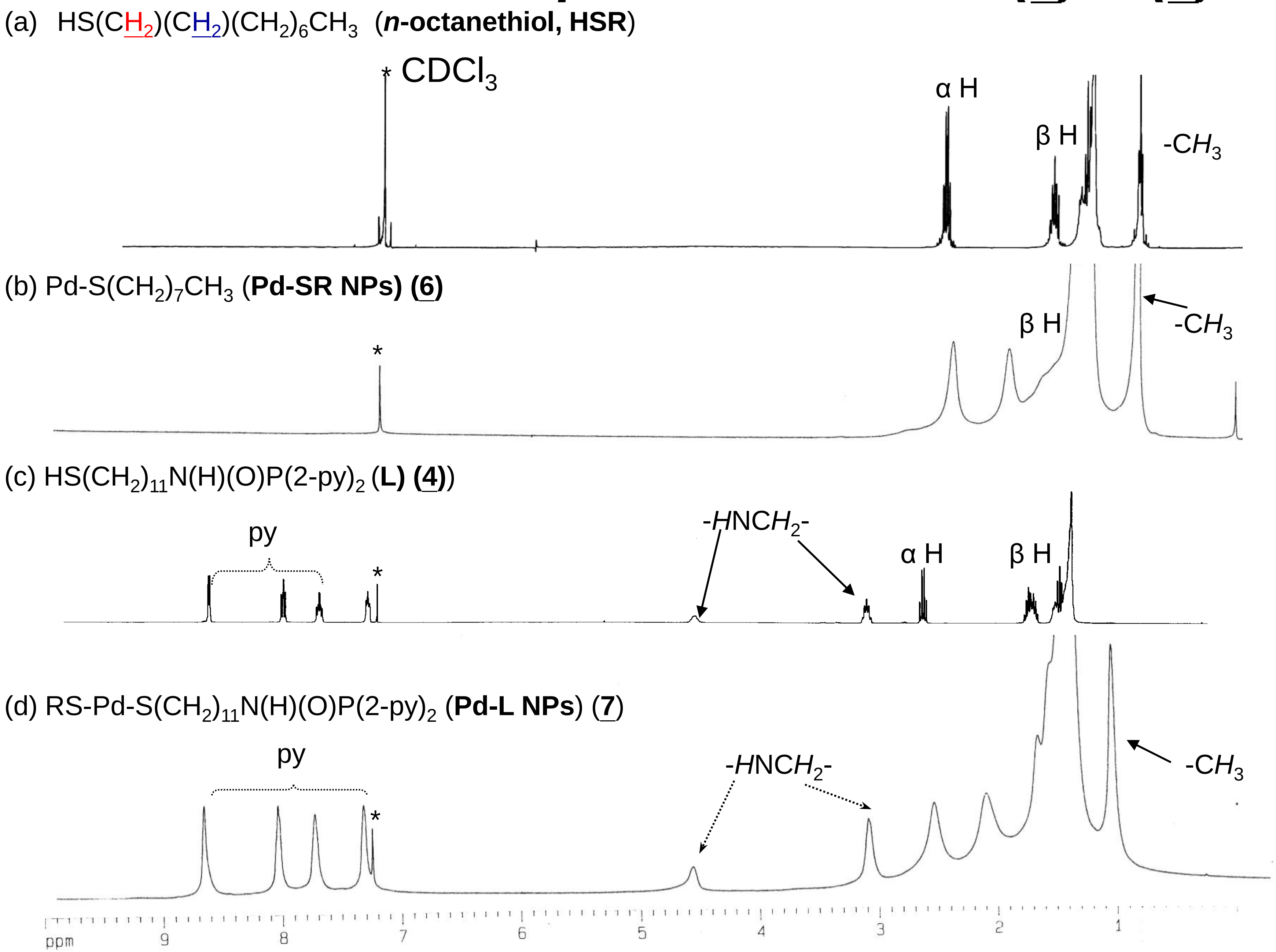
= 236 / 455 = 51.86 %

※經^{1}H-NMR定量得知在15.4 mg的Pd-L-$PdCl_2$ (8)
含有辛硫醇 1.77 mg。
含有Pd(II)錯化合物 10.56 mg
鈀奈米粒子重 = 3.07 mg
總鈀奈米粒子數
= 3.07 mg ÷ 106420 mg / mol × 6.02 × 10^{23} atom/mol ÷ 455 atom/particle
= 7.96 ×10^{15} particles
辛硫醇分子總數
= 1.77 mg ÷ 146000 mg / mol × 6.02 × 10^{23} atom/mol = 7.29 × 10^{18} atom
Pd(II)錯化合物總數
= 10.56 mg ÷ 580000 mg / mol × 6.02 × 10^{23} atom/mol = 1.09 × 10^{19} atom
單顆鈀奈米粒子表面含：
表面鈀原子數 = 203 atom
每一顆Pd NPs含有:
Pd(II)錯化合物:1.09 × 10^{19} atom÷(7.96×10^{15} particles)= 1369 atom/particle
辛硫醇= 7.29 × 10^{18} atom÷(7.96×10^{15} particles)= 915 atom/particle

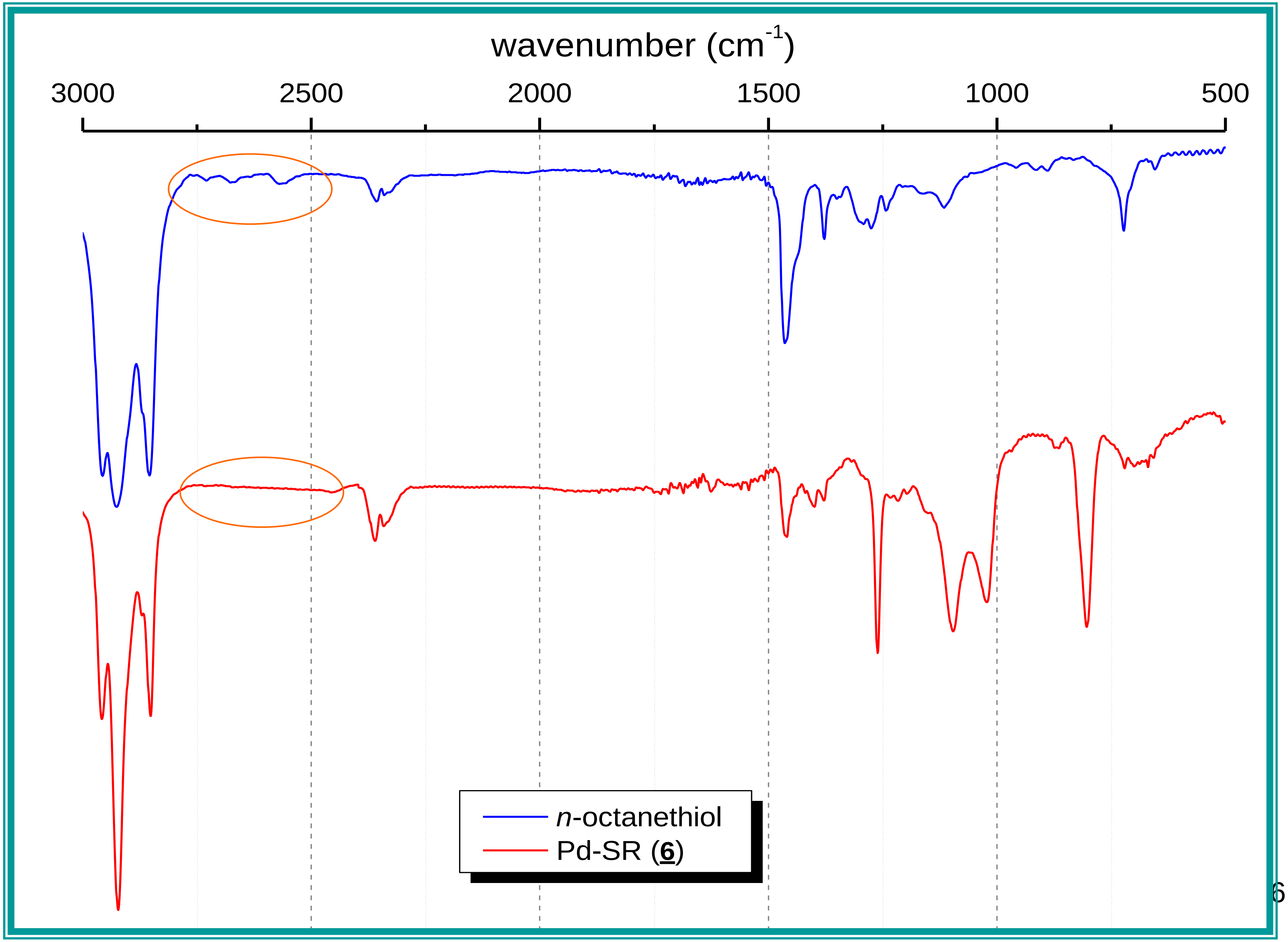
Analytical data of Pd Nanoparticles (6), (7) & (8)

Nanoparticle	Size (nm)	n-octanethiol / Ligand (4) (mole ratio)
Pd-SR (6)	2.60 ± 0.5	10 / 0
Pd-ligand (7)	2.72 ± 0.5	9.1 / 13.6
Pd-ligand-$PdCl_2$ (8)	2.41 ± 0.5	4.5 / 6

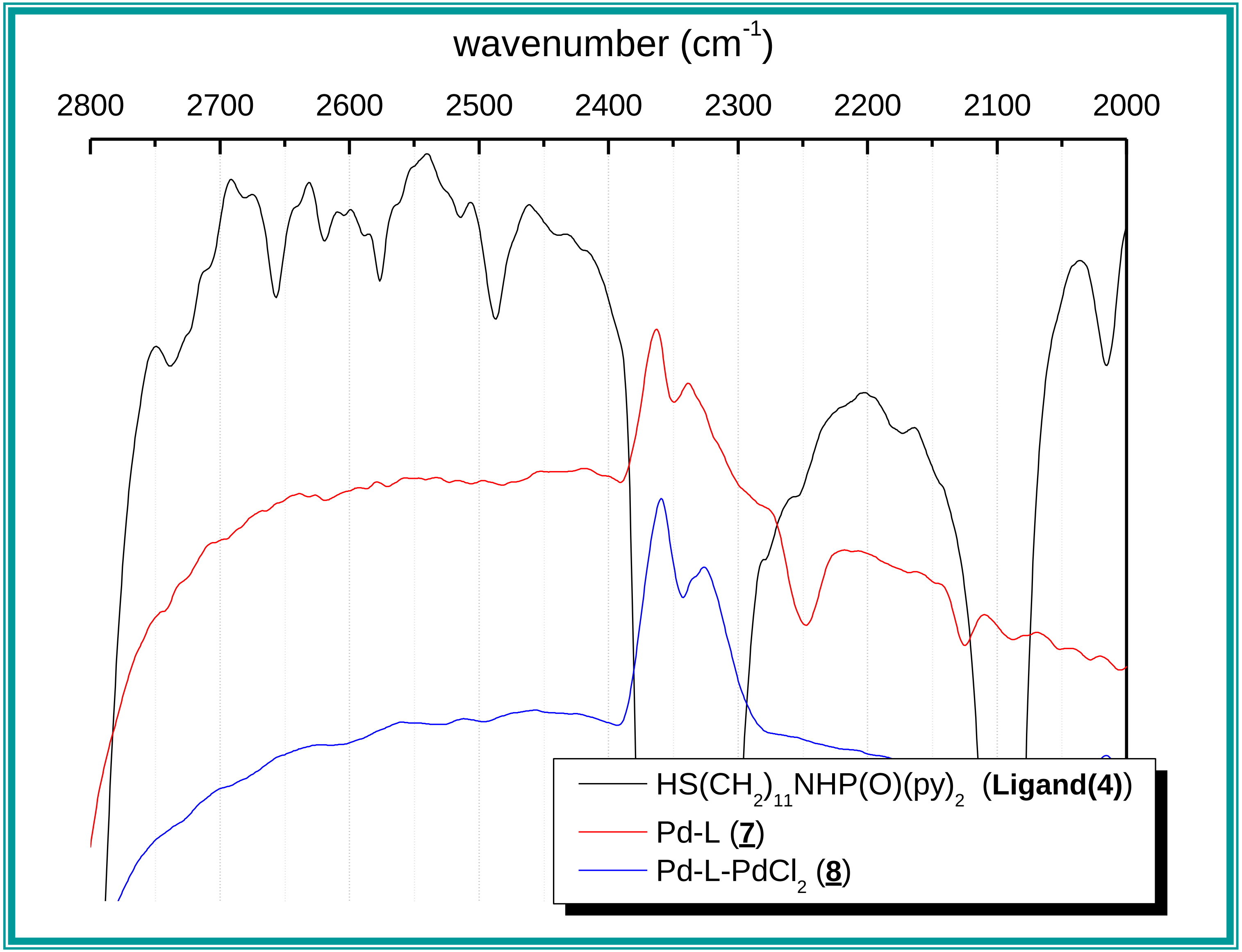
Solution ^{1}H NMR Spectra of Pd NPs (6) & (7)



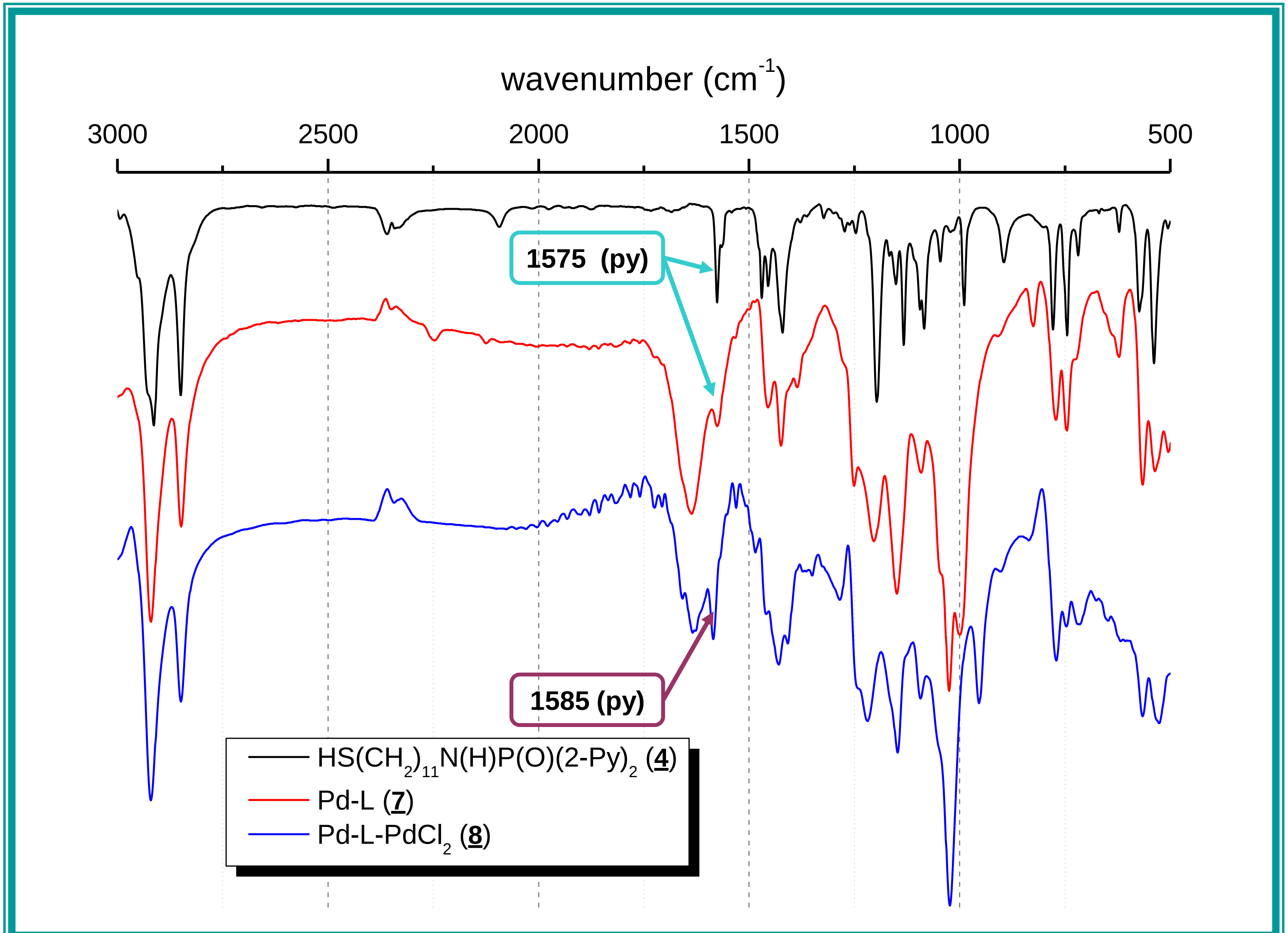
IR Spectra of n-Octanethiol & Pd-SR NPs (6)



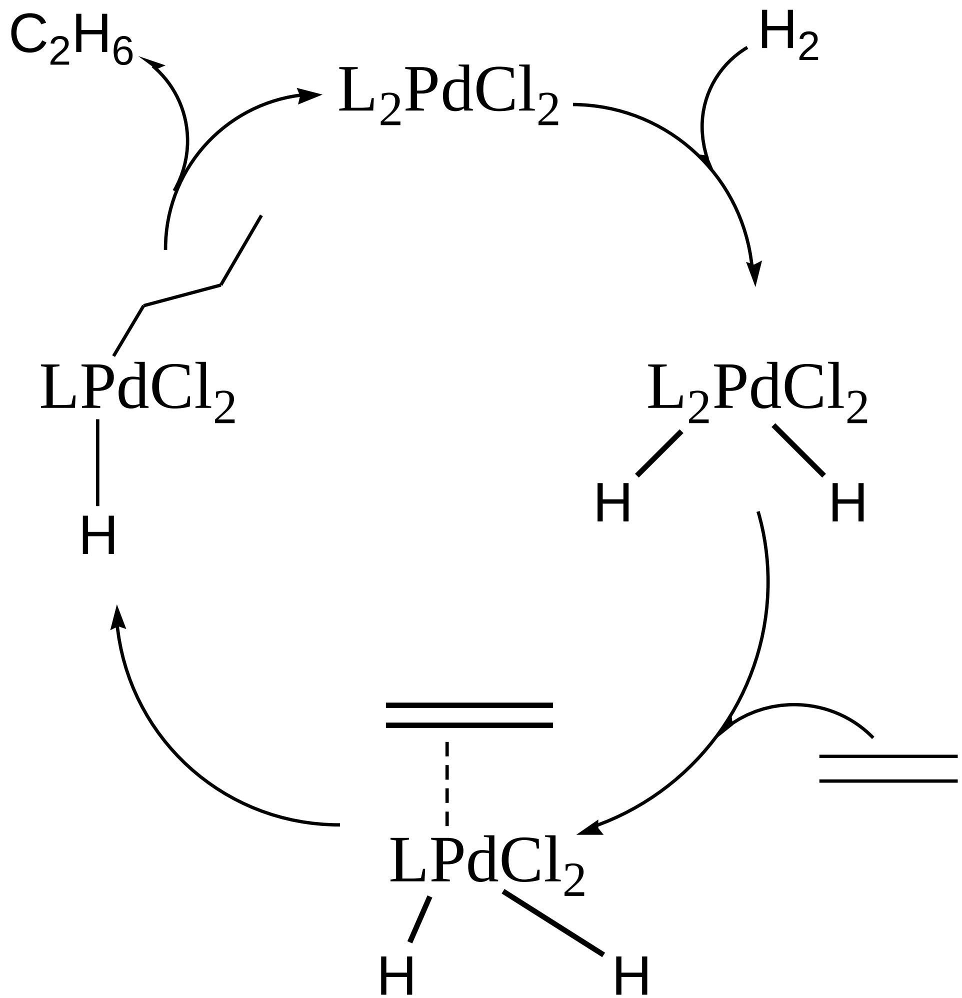
IR Spectra of Ligand (4), Pd NPs (7) & (8)



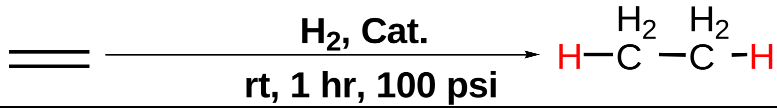
IR Spectra of Ligand (4), Pd NPs (7) & (8)



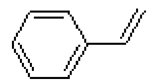
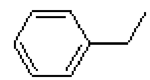
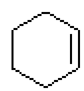
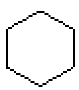
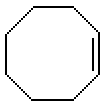
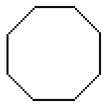
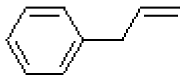
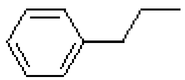
Hydrogenation Mechanism



Catalytic Hydrogenation Reactions in Hexane

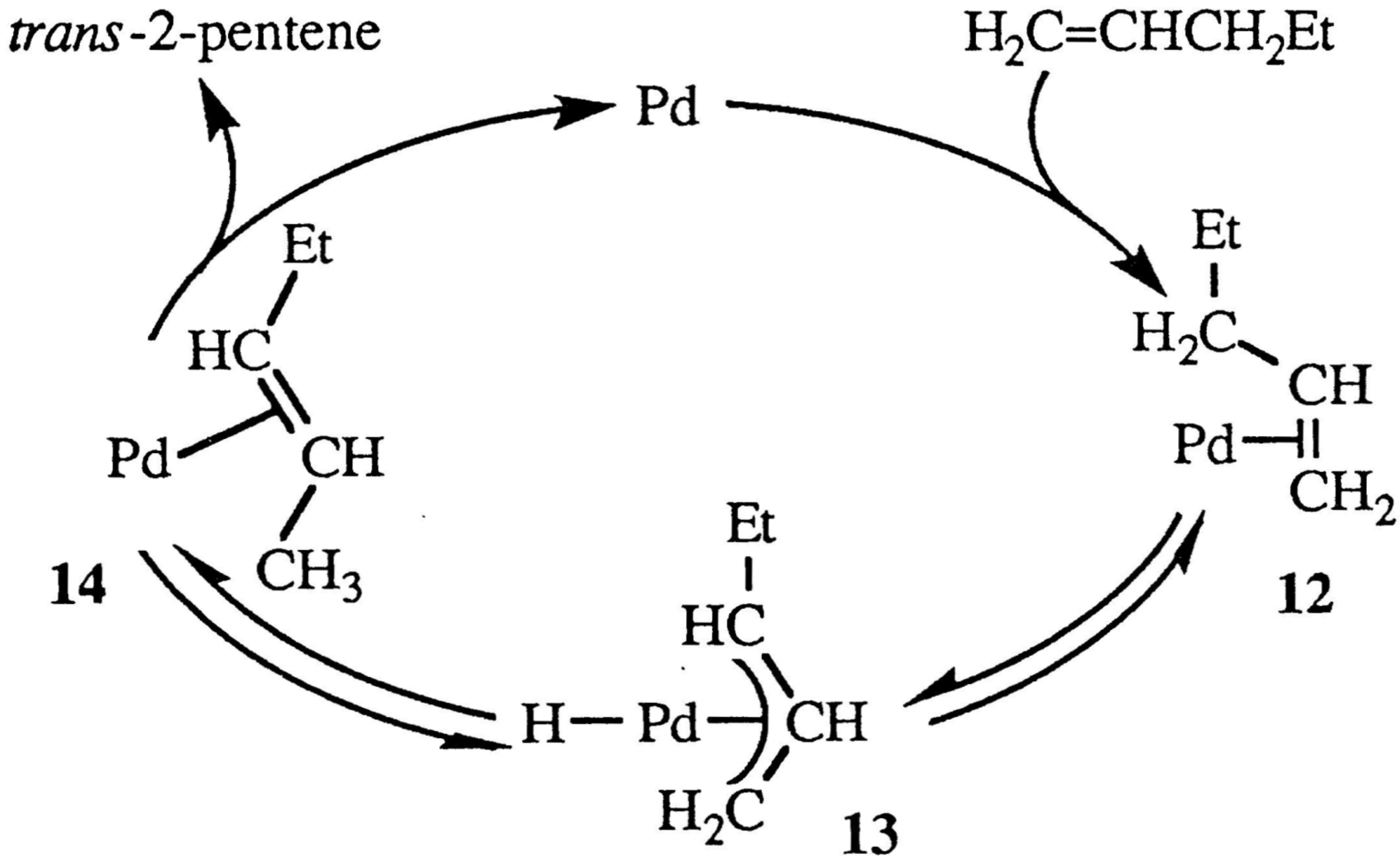


In Hexane

Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %
Pd-SR (**6**)			0.048[a]	1.0	92
			0.48[b]	1.0	67
			0. 48[b]	1.0	4
			0.16[c]	1.0	100 (18)

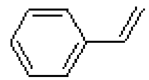
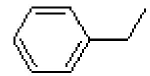
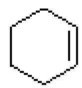
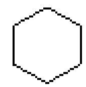
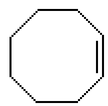
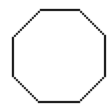
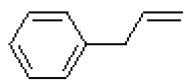
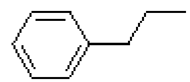
[a] Cat. = 0.3 mg, [b] Cat. = 3.0 mg, [c] Cat. = 1.0 mg
substrate = 3 mmol

Isomerization Mechanism

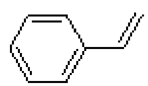
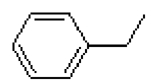
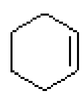
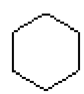
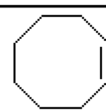
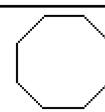
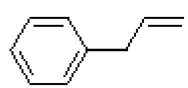
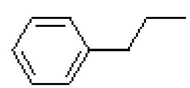


Hydrogenation Reactions in Various Solvent Systems

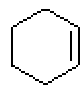
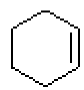
In Hexane
(homo.)

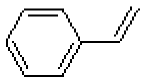
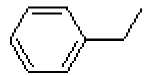
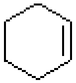
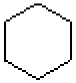
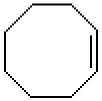
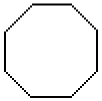
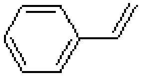
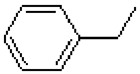
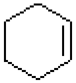
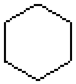
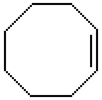
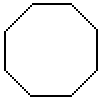
Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %
Pd-SR (**6**)			0.048	1.0	92
			0.48	1.0	67
			0.48	1.0	4
			0.16	1.0	100 (18)

In Ethanol
(hetero.)

Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %
Pd-SR (**6**)			0.08	1.0	99
			0.48	1.0	80
			0.16	1.0	6.5
			0.16	1.0	100 (34)

$PdCl_2(CH_3CN)_2$ vs Pd-L-$PdCl_2$ in Hydrogenation

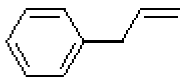
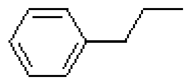
Cat.	substrate	mg (Pd(II)含量)	Reaction time (hr)	conv%
$PdCl_2(CH_3CN)_2$		0.0023 mg ($9*10^{-3}$ mmol)	1.0	43
Pd-L-$PdCl_2$		0.0050 mg ($9*10^{-3}$ mmol)	1.0	42

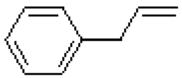
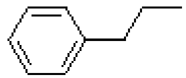
Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %
Pd-SR(**6**)			0.16[a]	1.0	99
			0.16[a]	1.0	59
			0.16[a]	1.0	6.5
Pd-L-$PdCl_2$ (**8**)			0.03[a] (0.06)	1.0	99
			0.03[a] (0.06)	1.0	59
			0.03[a] (0.06)	1.0	N.R.

[a] Cat. = 1.0 mg, solvent system: ethanol

substrate = 3 mmol

Hydrogenation and Isomerization Reactions

Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %	isomerization
Pd-SR(**6**)			0.16[a]	1.0	100 (52)	→ 48
			0.16[a]	1.0	100 (34)	→ 66

Cat.	substrate	product	Pd_{surf} mol %	Reaction time (hr)	conv %	
$Pd\text{-}L\text{-}PdCl_2$ (**8**)			0.03[a] (0.06)	1.0	100 (56)	→ 44
			0.03[a] (0.06)	1.0	100 (38)	→ 62

[a] Cat. = 1.0 mg,solvent system: ethanol

Conclusions

- We have developed a method to successfully immobilize molecular Pd(II) complexes catalysts on the surfaces of Pd NPs.
- Since the Pd NPs-Pd(II) hybrid catalysts are highly soluble in organic solvents, their structures and reactions could be easily studied by simple solution NMR technique.
- The Pd NPs-Pd(II) complexes were proven to be catalysts for a series of hydrogenation and isomerization reactions.