Solid-supported Organometallic Catalysts

2016. 4. 9

Haruka Fujino

Prof. Masaya Sawamura (澤村正也教授)

Education:

1980-1984 B.Sc., Kyoto Univesity (Prof. Yoshihiko Ito/伊藤嘉彦教授)
1984-1989 Ph.D., Chemistyr from Kyoto University (Prof. Yoshihiko Ito/伊藤嘉彦教授)

Appointments:

1989-1995 Assistant Professor, Kyoto Univerisity (Prof. Yoshihiko Ito/伊藤嘉彦教授)
1993-1994 Visiting Researcher, Harvard University (Prof. Stuart L. Schreiber)
1995 Assistant Professor, Tokyo Institute of Technology (Prof. Eiichi Nakamura/中村栄一教授)
1995-1996 Assistant Professor, The University of Tokyo (Prof. Eiichi Nakamura/中村栄一教授)
1996-1997 Lecture, The University of Tokyo (Prof. Eiichi Nakamura/中村栄一教授)
1997-2001 Associate Professor, The University of Tokyo (Prof. Eiichi Nakamura/中村栄一教授)
2001-present Professor, Hokkaido University (PI/研究室主宰者)

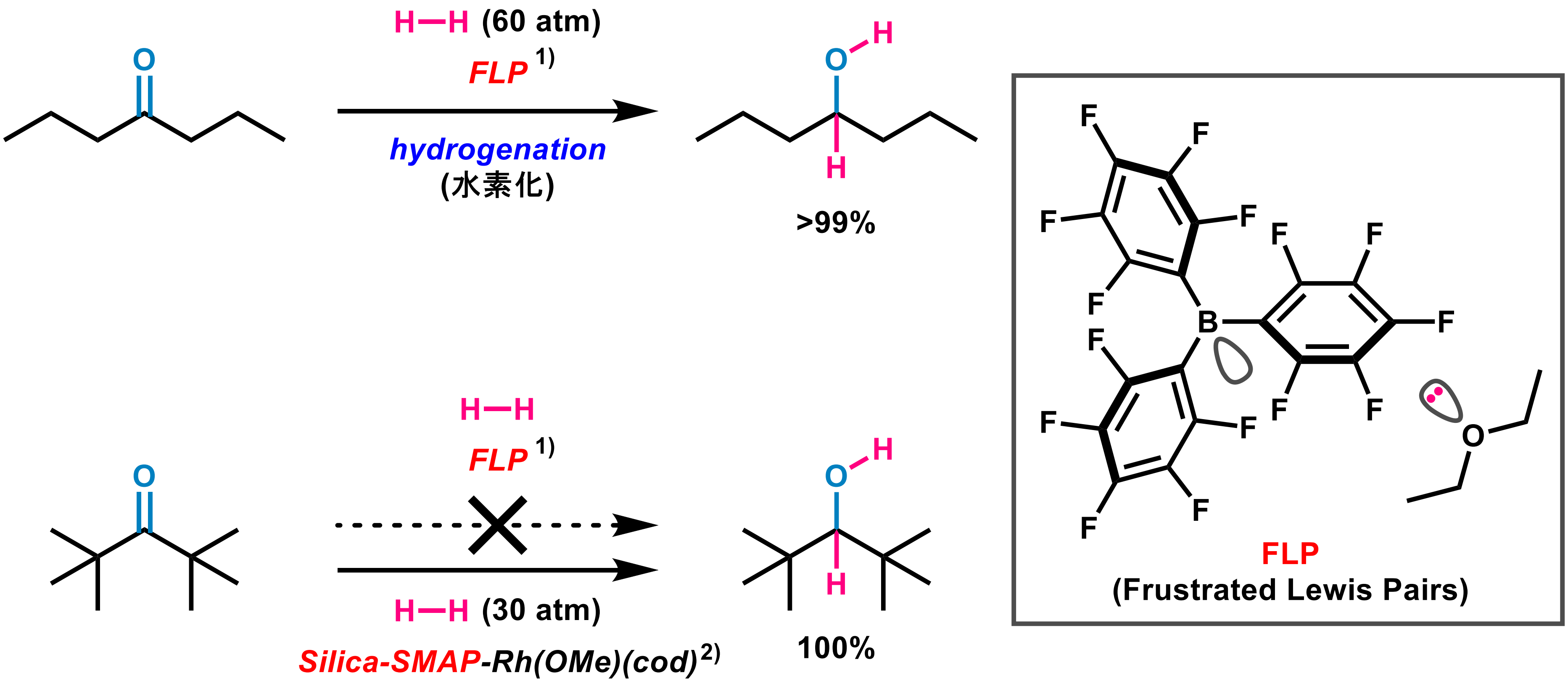
Awards:

1990 Elzai Award Synthetic Organic Chemistry, Japan
1996 The Chemical Society of Japan Award for Young Chemists
2007 OMCOS Poster Priza in Organometallic Chemistry
2008 Visiting Lectureship Award from National Scienece Council, Taiwan
2009 Asian Core Program (ACP) Lectureship Award (2009)
2012 Chemical Society of Japan Award for Creative Work
2012 Asian Core Program (ACP) Lecture ship Award (2012)
2013 Asian Core Program (ACP) Lecture ship Award (2013)
2014 Hokkaido University President's Award for Outstanding Reserach
2015 SSOCJ Nissan Chemical Industries Award for Novel Reaction and Method 2014

Editors:

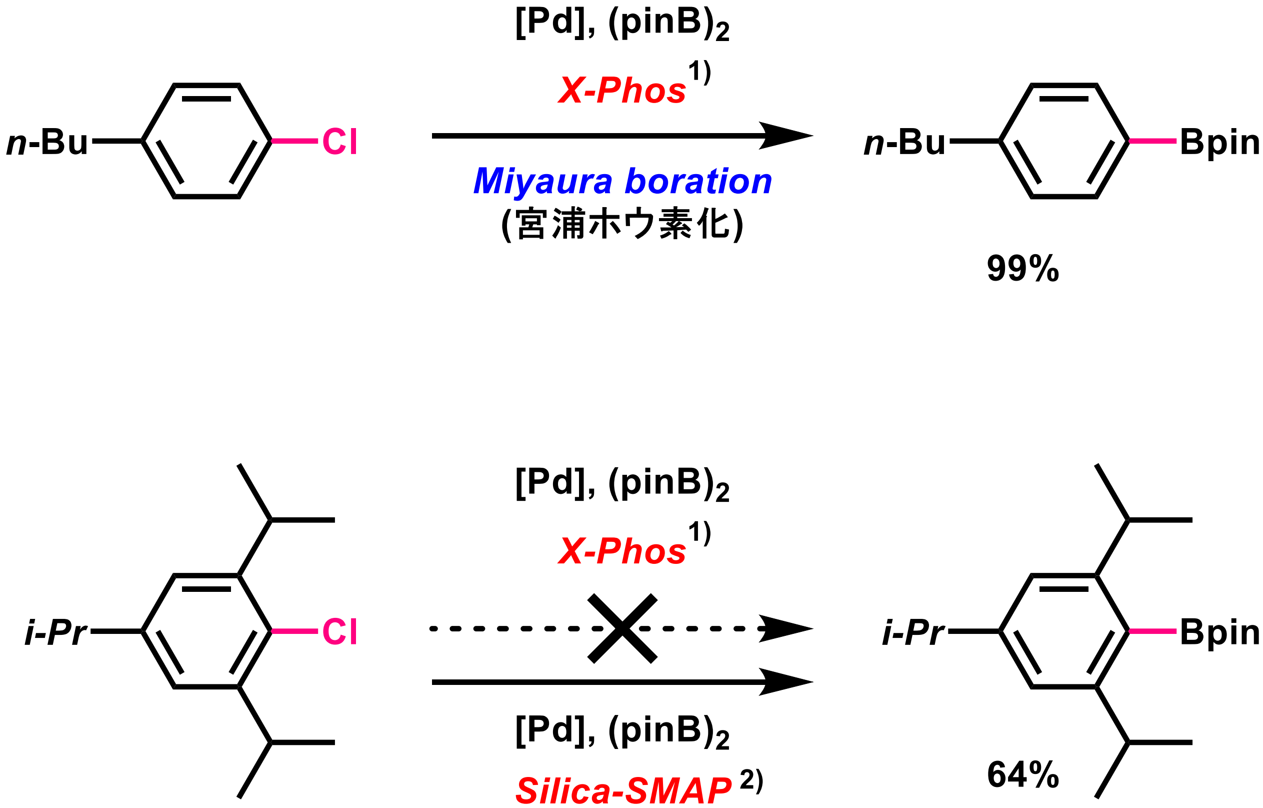
Tetrahedron, Consulting Editor
Tetrahedron Letters, Consulting Editor

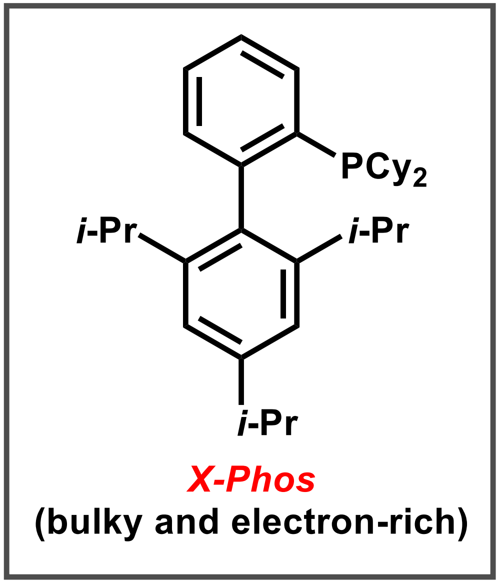
What Can Be Realized by Prof. Sawamura's Research? (1)



1. Mahdi, D.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 15809.; Related LS: 150131_Hiroyuki_Mutoh.
2. Kawamorita, S.; Hamasaka, G.; Ohmiya, H.; Hara, K.; Furuoka, A.; Sawamura, M. *Org. Lett.*, **2008**, *10*, 4697.

What Can Be Realized by Prof. Sawamura's Research? (2)





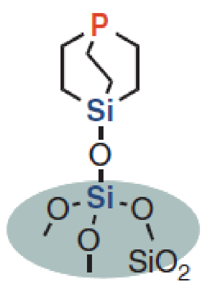
1. Billingsley, T. E.; Barder, T. E.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 5359.
2. Kawamorita, S.;Ohmiya, H.; Iwai. T.; Sawamura, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 8363.

Contents

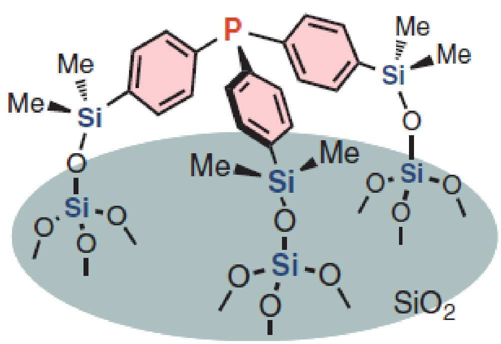
1. Introduction of solid-supported catalyst

2. Study 1; Site-isolation

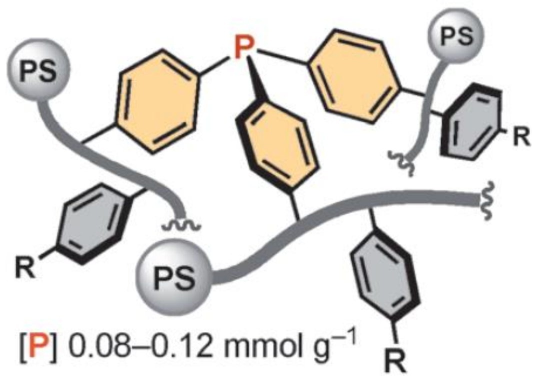
2.1 Silica-SMAP



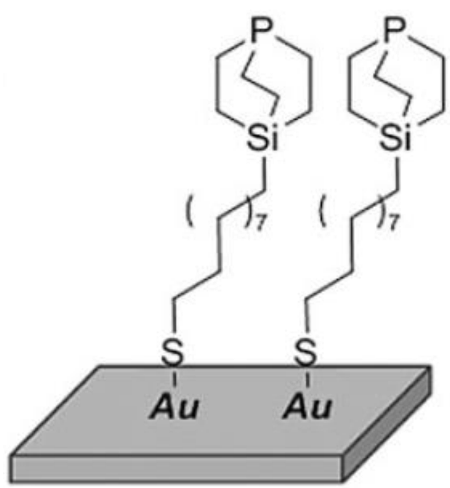
2.2 Silica-3p-TPP



2.3 PS-Ph_3P

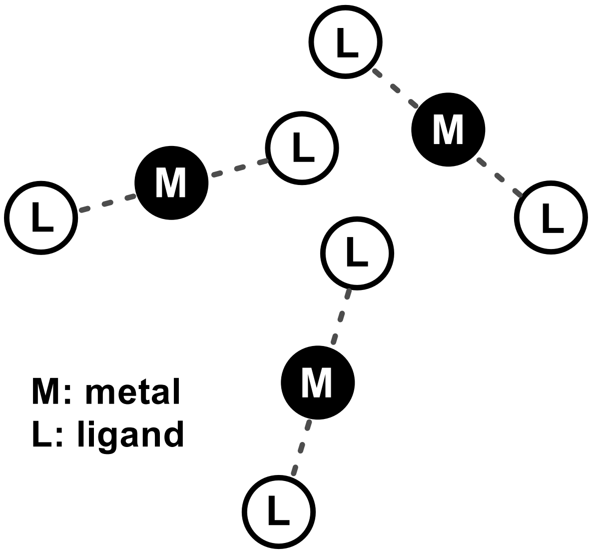


3. Study 2; Self-assembled monolayers



Contents

Organometallic Catalysts



homogeneous catalysts
(均一系触媒)

✓ high activity/selectivity
✓ tuning by various ligands

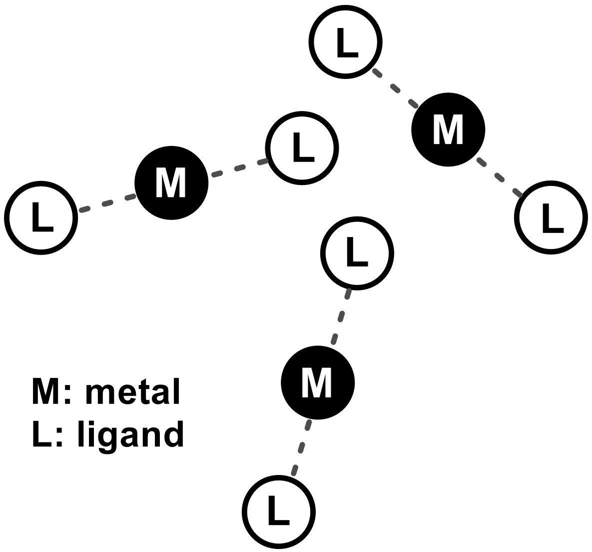
ex. Wilkinson catalyst

heterogeneous catalysts
(不均一系触媒)

✓ saparation
✓ recycling

ex. Pd/C

Organometallic Catalysts



M: metal
L: ligand

homogeneous catalysts
(均一系触媒)

✓ high activity/selectivity
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ex. Wilkinson catalyst

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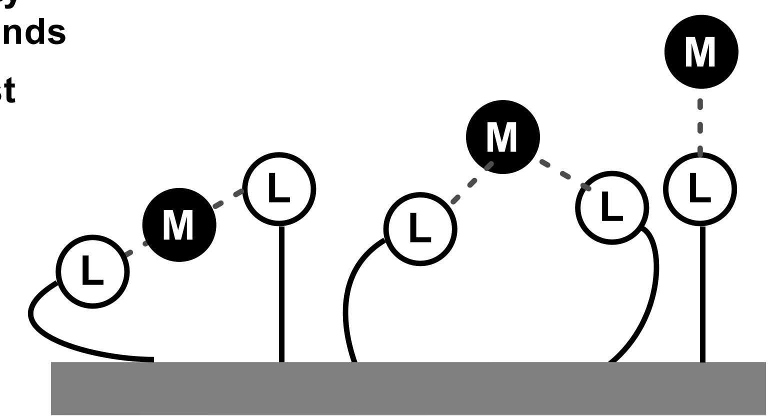
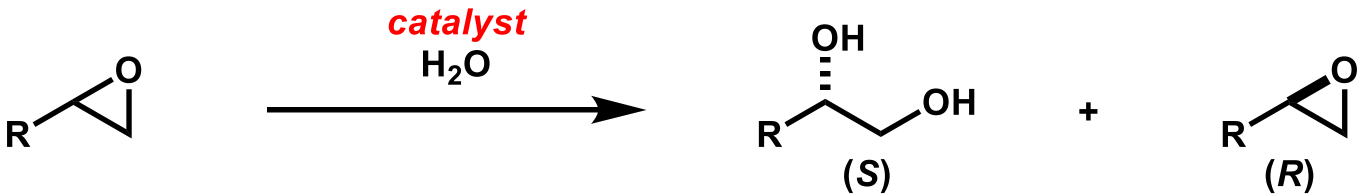
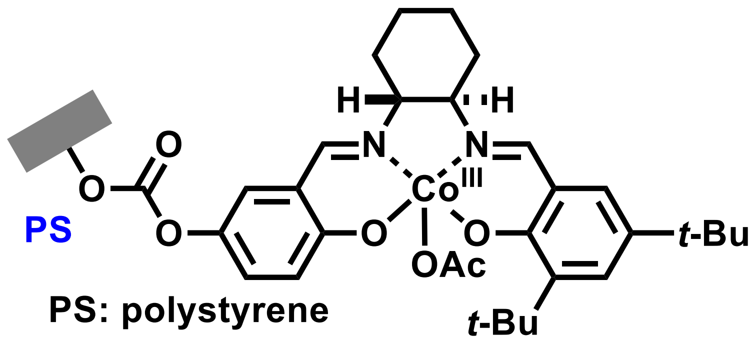
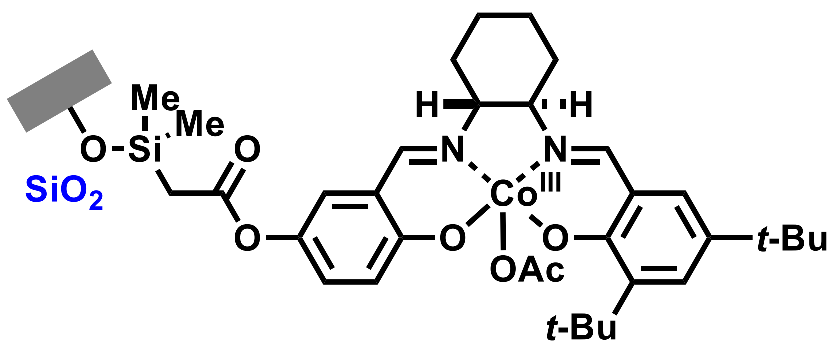
ex. Pd/C



solid-supported organometallic catalysts
(固相担持有機金属触媒)

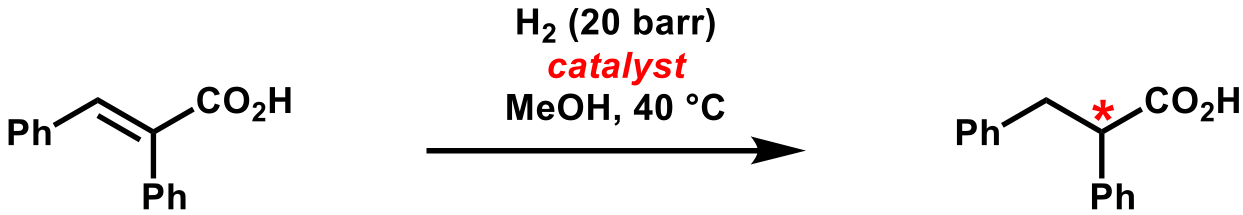
One exapmle of Solid-supported Catalysts (1)[1]



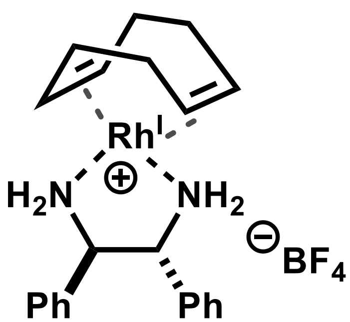
R	catalyst	Yield of (*S*)	*ee* of (*S*)
$(CH_2)_2OH$	(*R*,*R*)-salenCoOAc	43%	98%
		36%	93%
Ph	(*R*,*R*)-salenCoOAc	32%	96%
		50%	96%

1. Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 4147.

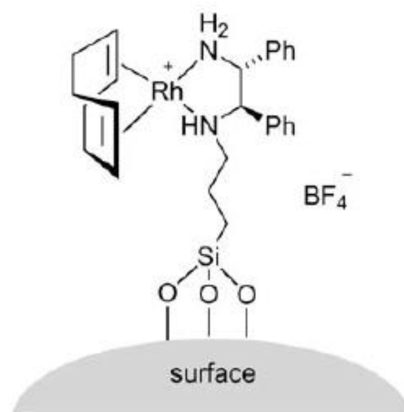
One exapmle of Solid-supported Catalysts (2)[1]



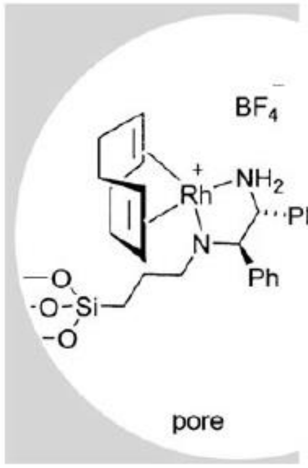
catalysts



$[Rh(cod)dpen]BF_4$
95%, 79%*ee*



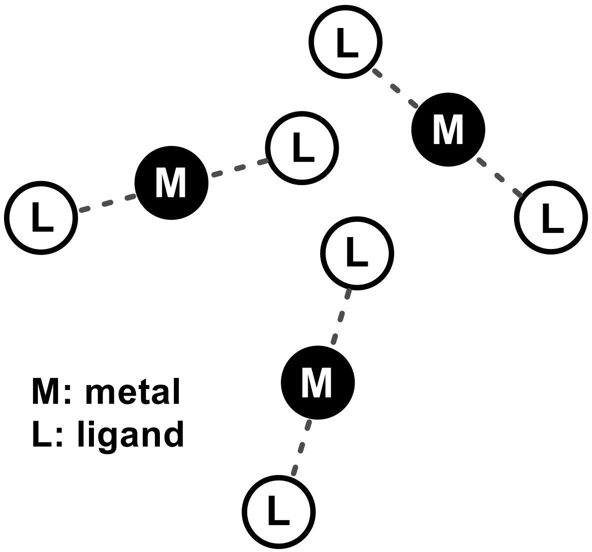
on carbosil (nonpororus)
95%, 79%*ee*



on MCM-41 (mesoporous)
75%, 88%*ee*

1. Jones, M. D.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Vaughen, D. E. W.; *Angew. Chem. Int. Ed.* **2003**, *42*, 4326.

Organometallic Catalysts



homogeneous catalysts
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- ✓ high activity/selectivity
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ex. Wilkinson catalyst

heterogeneous catalysts
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- ✓ saparation
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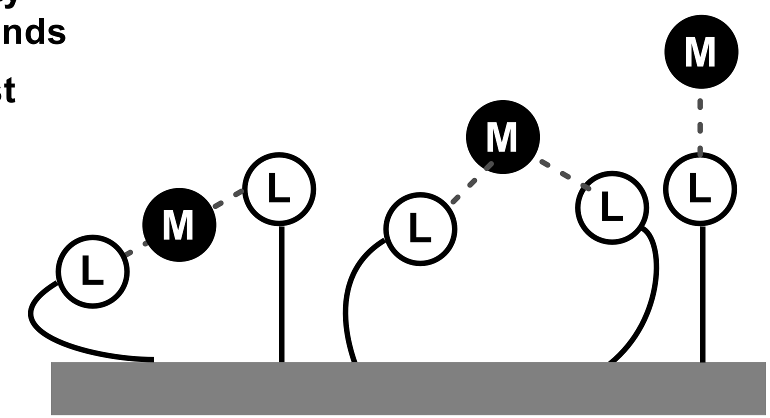
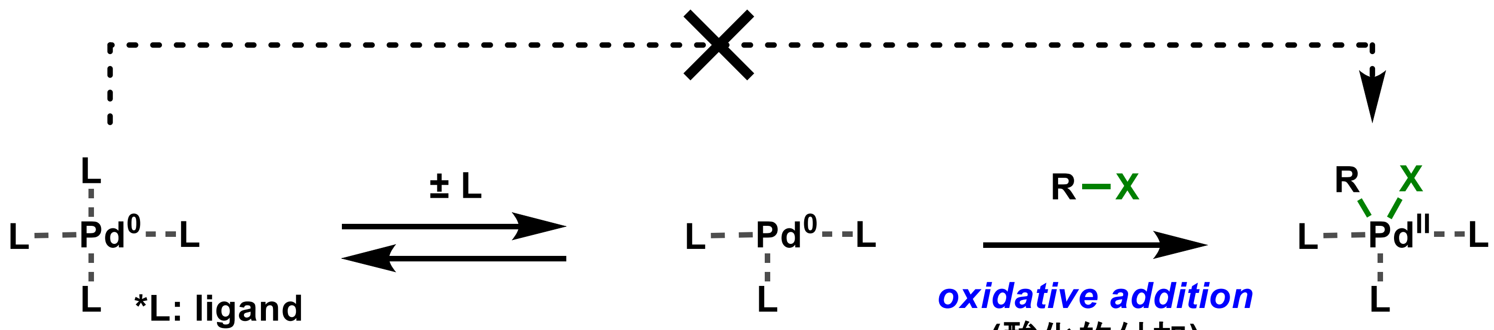


solid-supported organometallic catalysts
(固相担持有機金属触媒)

Coordinative Saturation/Unsaturation

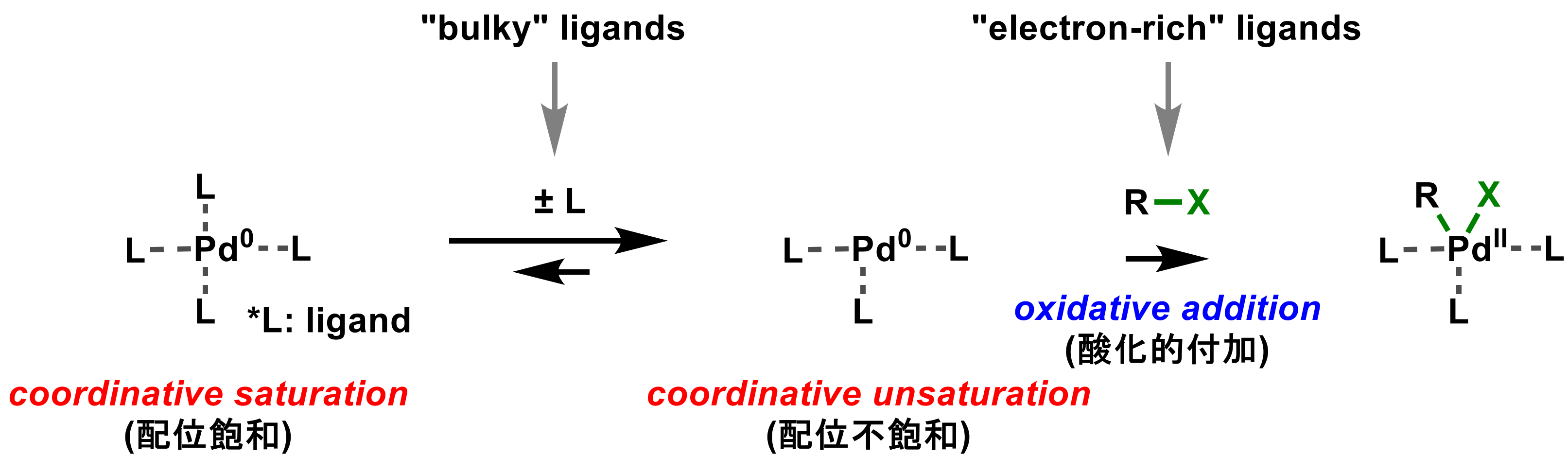


coordinative saturation
(配位飽和)

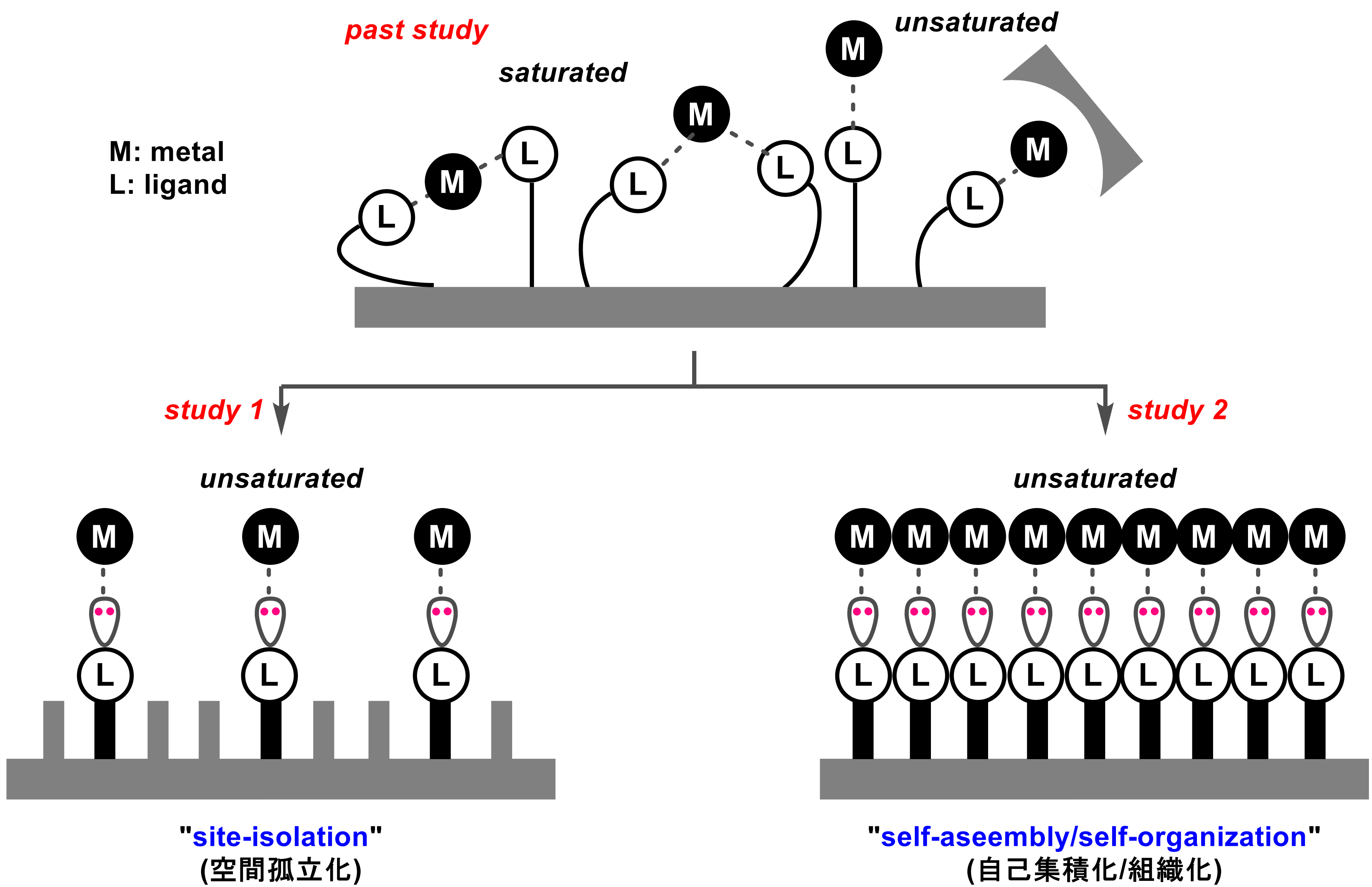
coordinative unsaturation
(配位不飽和)

oxidative addition
(酸化的付加)

Coordinative Saturation/Unsaturation



Outline of Prof. Sawamura's Unsaturated Complex



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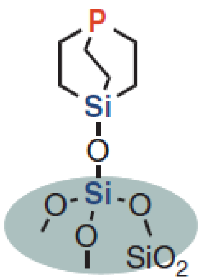
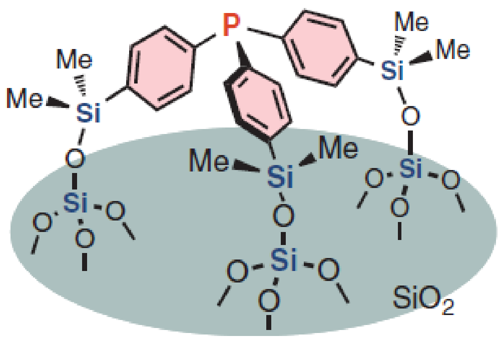
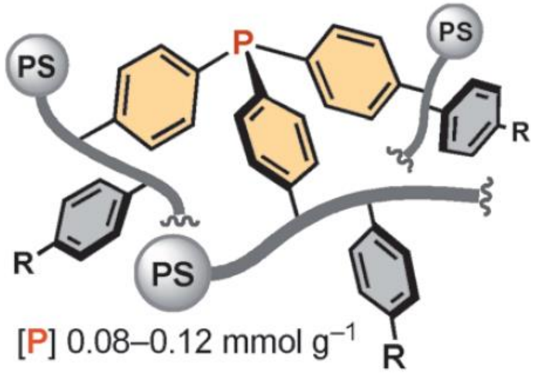


2.2 Silica-3p-TPP



2.3 PS-Ph_3P

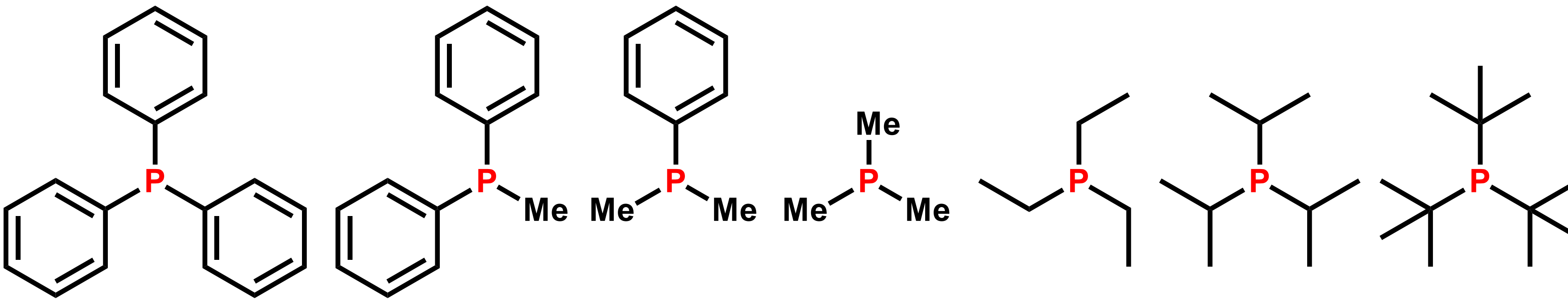


3. Study 2; Self-assembled monolayers

Phosphine Ligands

phosphine ligands

- ✓ high affinity to various metal species
- ✓ easy tuning by controlling electronic and steric nature of ligands
- × unstable to air (= easily oxidized)



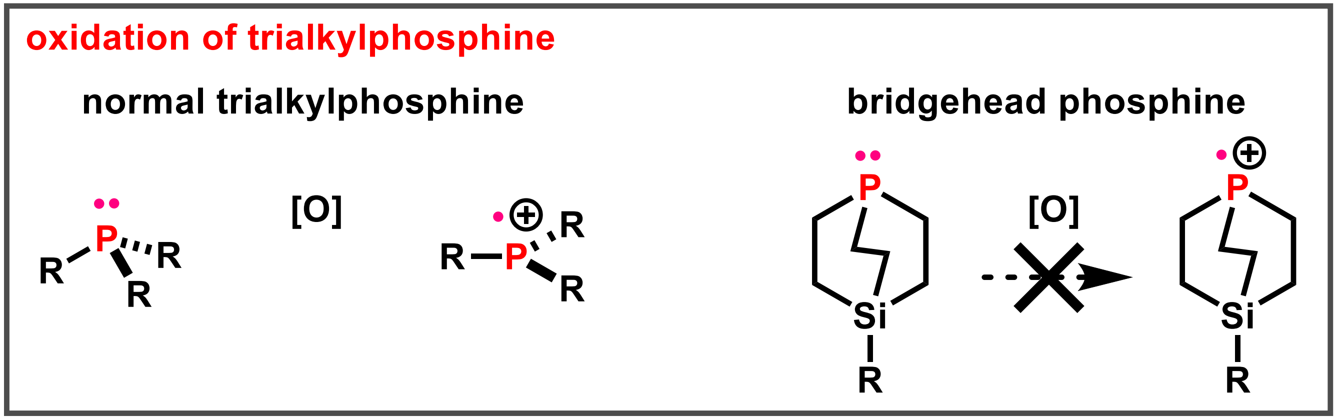
Vmin [1] (kcal/mol)	–34.85	–36.76	–40.41	–43.02	–43.51	–44.47	–45.48
C–P–C angle [2] (deg)	n/d	n/d	n/d	99.4	99.5	101.6	107.5

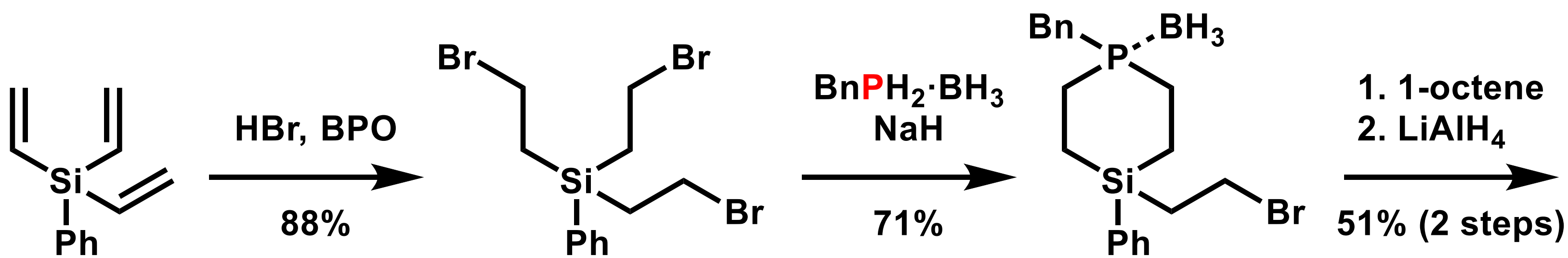
(*Vmin*: molecular electrostatic potential minimum)
(B3LYP/6-31G(d,p))

✓ *electron-donating ability*
× *unstability to air*

1. Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573.
2. (a) Ochida, A.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2003**, *5*, 2671.
(b) Ochida, A.; Ito, S.; Miyahara, T.; Ito, H.; Sawamura, M. *Chem. Lett.* **2006**, *35*, 294.

Design and Synthesis of "SMAP"[1]





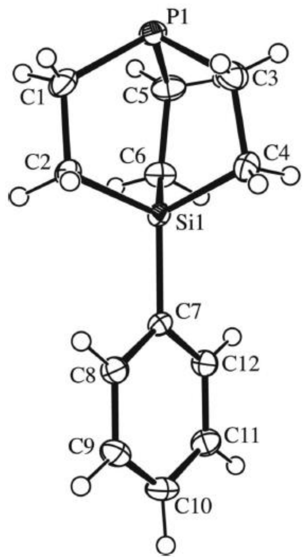
"SMAP"
silicon-constraines
monodentate
tri**a**lkyl**p**hosphine

✓ air-stable
✓ crystalline

1. (a) Ochida, A.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2003**, *5*, 2671.
(b) Ochida, A.; Ito, S.; Miyahara, T.; Ito, H.; Sawamura, M. *Chem. Lett.* **2006**, *35*, 294.
(c) Sawamura, M. *et al. Organometallics* **2008**, *27*, 5494.

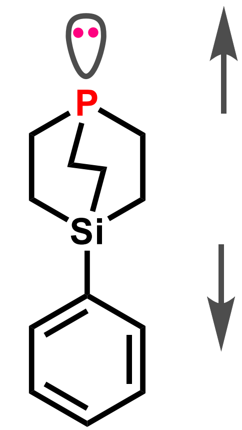
Property and Characteristics of SMAP[1)]

1. X-ray analysis



ORTEP drawing of Ph-SMAP

observed angle (deg)
C(1)–P(1)–C(3): 100.42
P(1)–C(1)–C(2)–Si(1): -15.3



Ph-SMAP

- ✓ electron-rich
- ✓ air-stable
- ✓ compact ligand
- ✓ rigid framework

2. DFT calculation

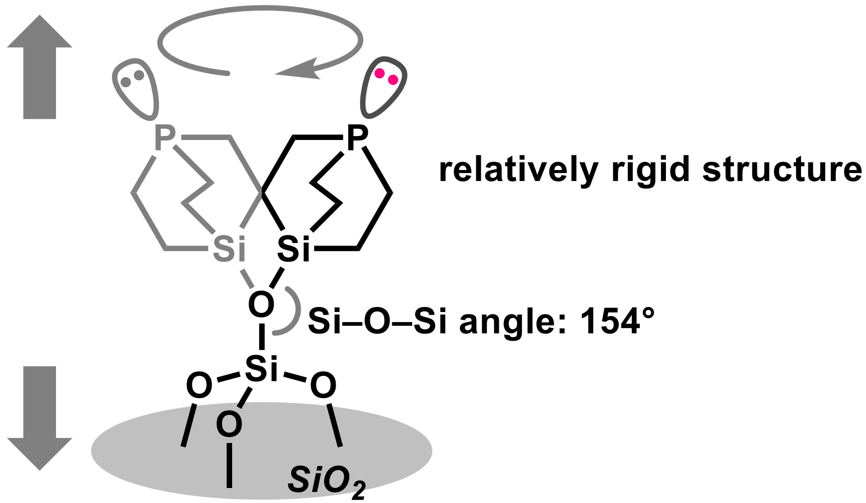
(B3LYP/6-31(d,p))	calcd. *Vmin* (kcal/mol)	calcd. C–P–C angle (deg.)
t-Bu_3P	–45.48	107.5
i-Pr_3P	–44.47	101.6
Et_3P	–43.51	99.5
Ph-SMAP	**–43.14**	**99.7**
Me_3P	–43.02	99.4
Me_2PhP	–40.41	n/d

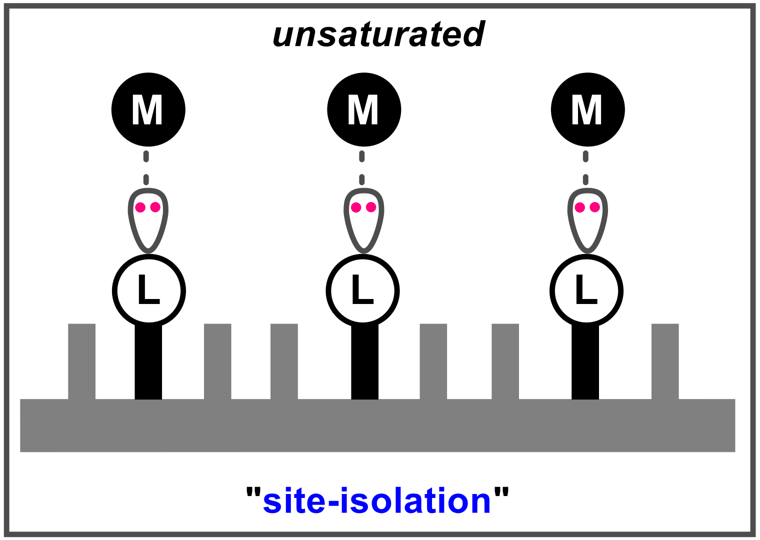
↑ *electron-donating*

1. (a) Ochida, A.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2003**, *5*, 2671.
(b) Ochida, A.; Ito, S.; Miyahara, T.; Ito, H.; Sawamura, M. *Chem. Lett.* **2006**, *35*, 294.
(c) Sawamura, M. *et al. Organometallics* **2008**, *27*, 5494.

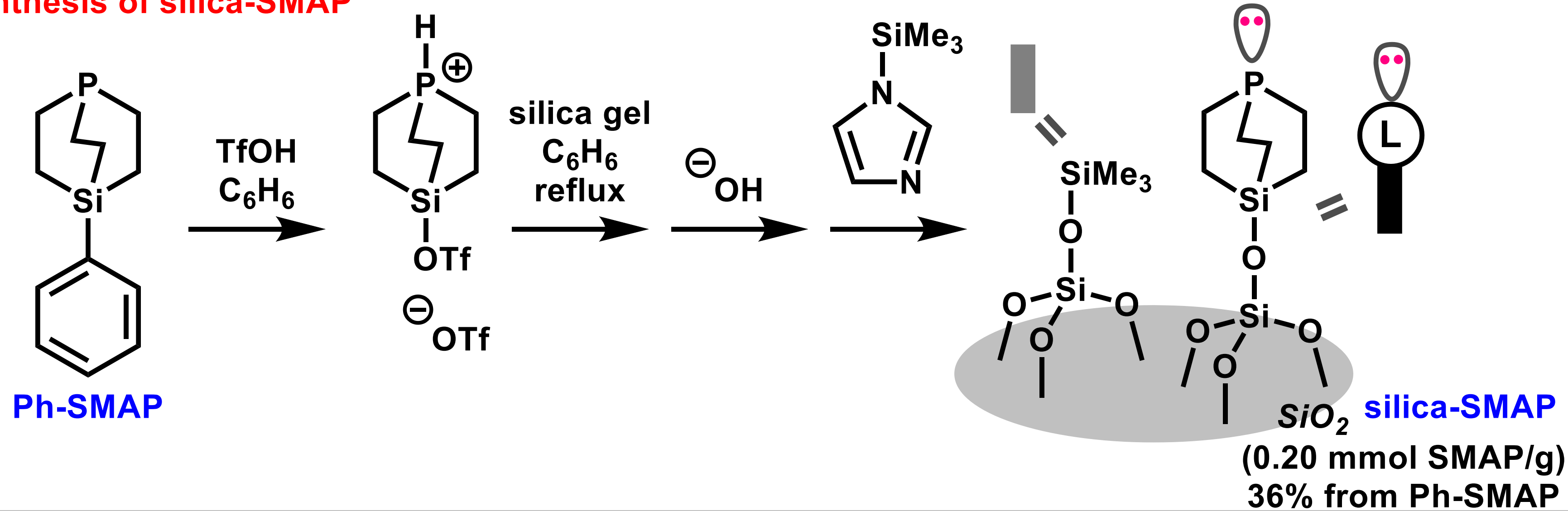
Design and Synthesis of Silica-SMAP[1)]

Restricted mobiliy of silica-SMAP





Synthesis of silica-SMAP



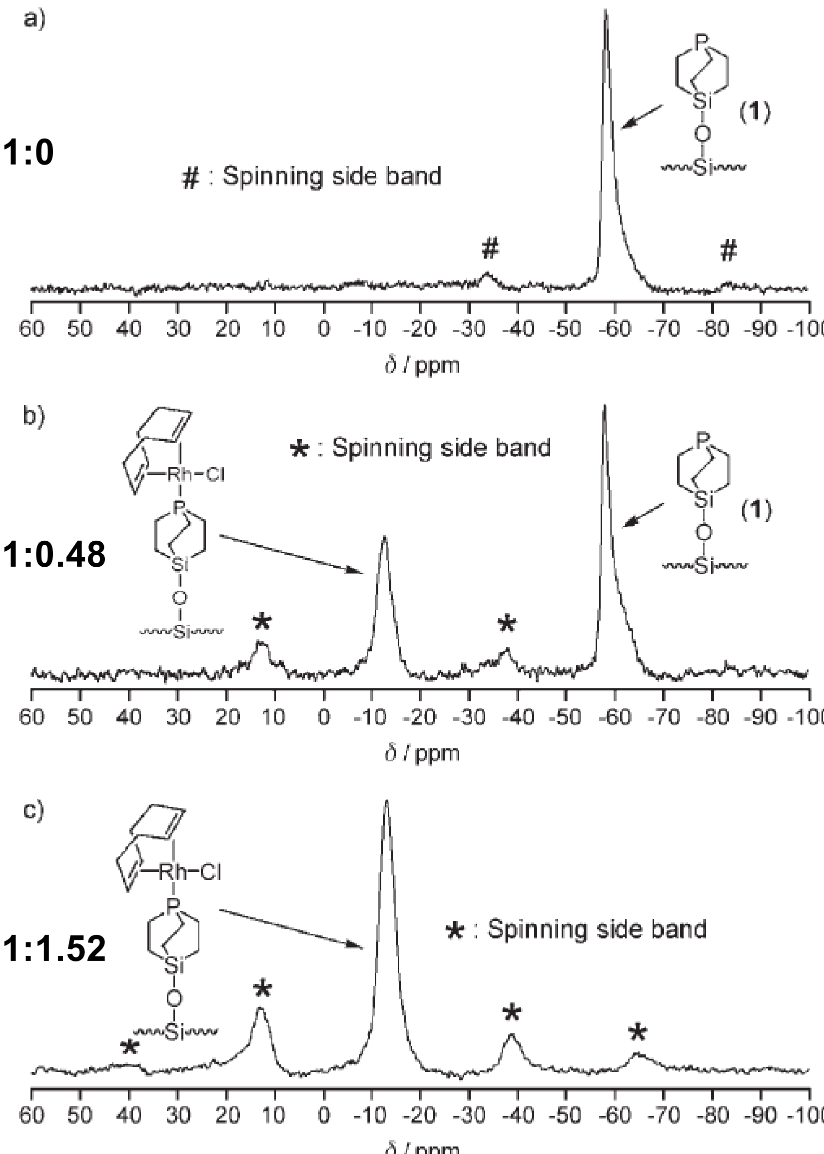
1. Hamasaka, G.; Ochda, A.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 5381.

Silica-SMAP Forms Unsaturated Complex[1)]

silica-SMAP/Rh = 1:0

silica-SMAP/Rh = 1:0.48

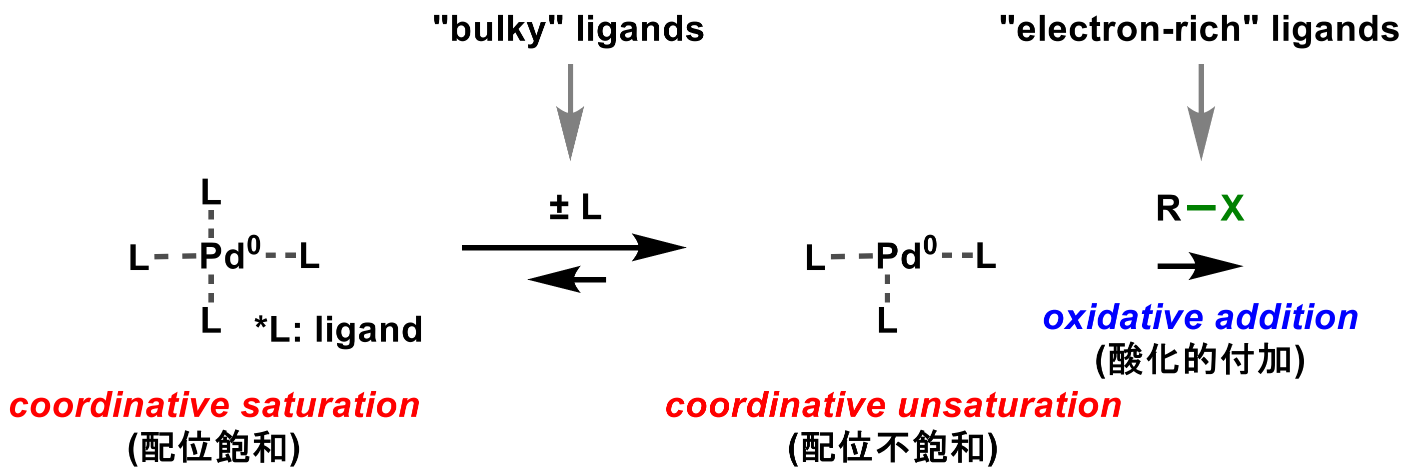
silica-SMAP/Rh = 1:1.52



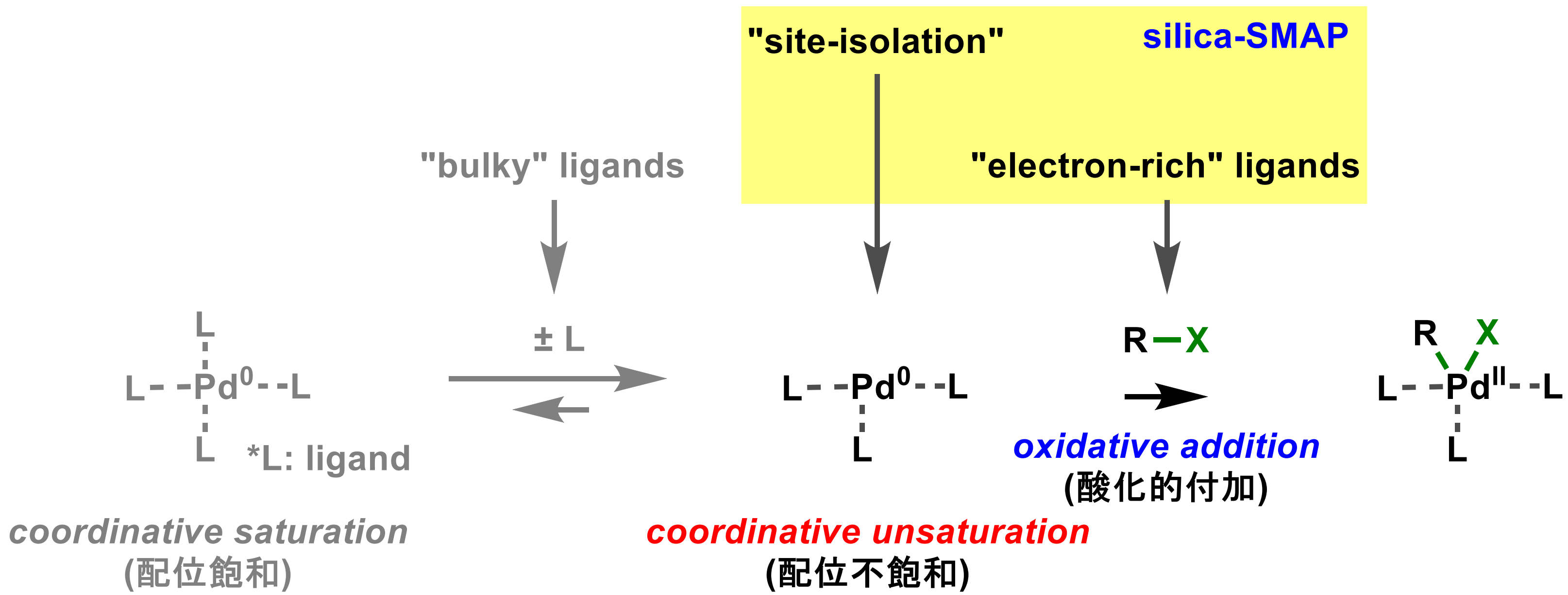
^{31}P CP/MAS NMR spectra

1. Hamasaka, G.; Ochda, A.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 5381.

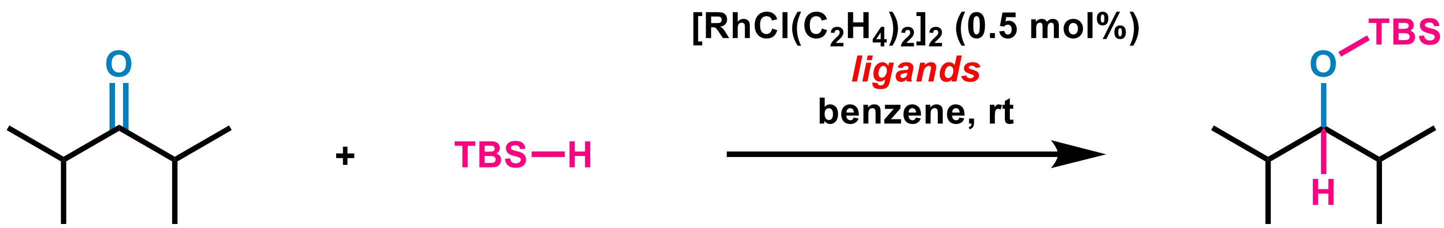
Coordinative Saturation/Unsaturation



Coordinative Saturation/Unsaturation



Hydrosilylation Catalyzed by Silica-SMAP[1)]



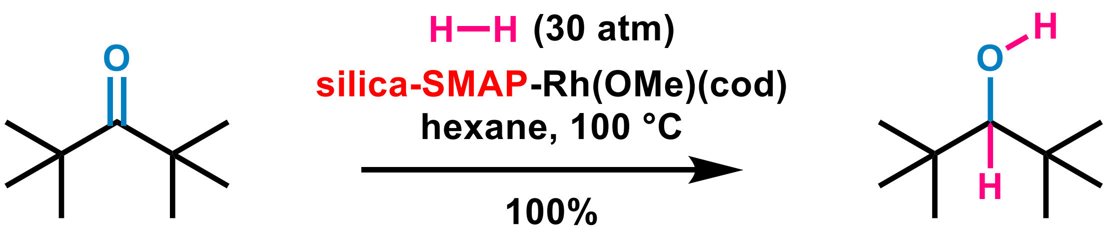
ligands	*ligands*/Rh	yield
PPh_3	1:1 or 1:2	<2%
t-Bu_3P	1:1 or 1:2	<2%
Ph-SMAP	1:1 or 1:2	<2%
silica-SMAP	**1:2**	**100%**
silica-SMAP	1:2	100% [a]

[a] after 6th run

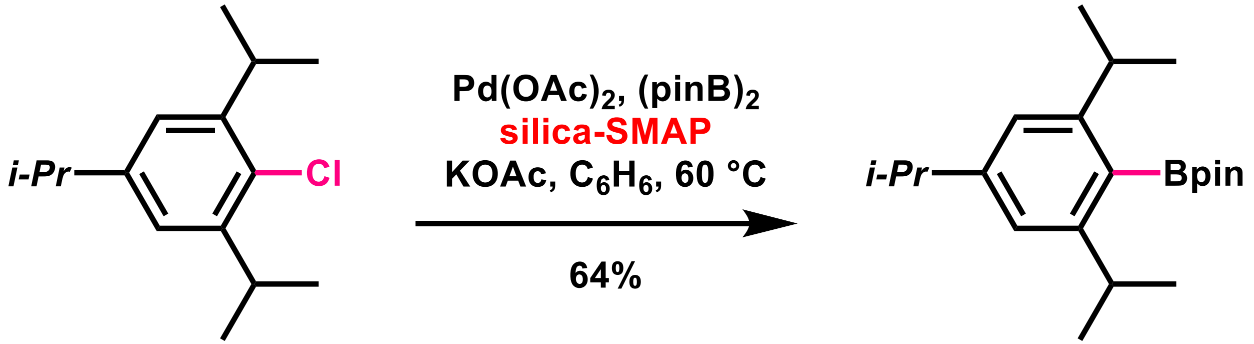
1. Hamasaka, G.; Ochda, A.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 5381.

Other Reactions Catalyzed by Silica-SMAP

hydrogenation[1)]

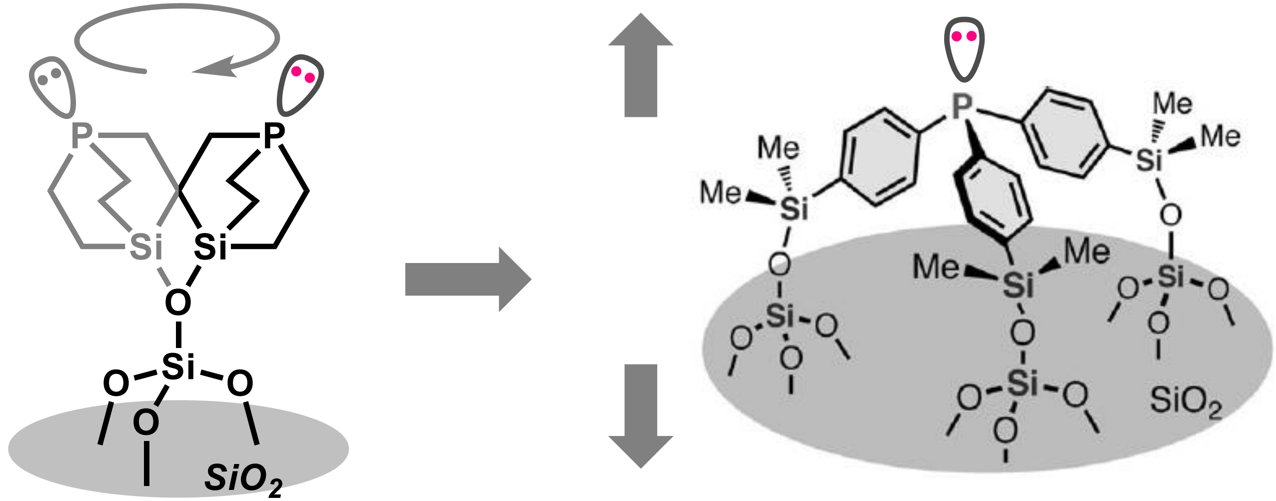


Miyaura-boration[2)]



1. Kawamorita, S.; Hamasaka, G.; Ohmiya, H.; Hara, K.; Furuoka, A.; Sawamura, M. *Org. Lett.*, **2008**, *10*, 4697.
2. Kawamorita, S.;Ohmiya, H.; Iwai. T.; Sawamura, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 8363.

Threefold Linked Ligand "Silica-3p-TPP"

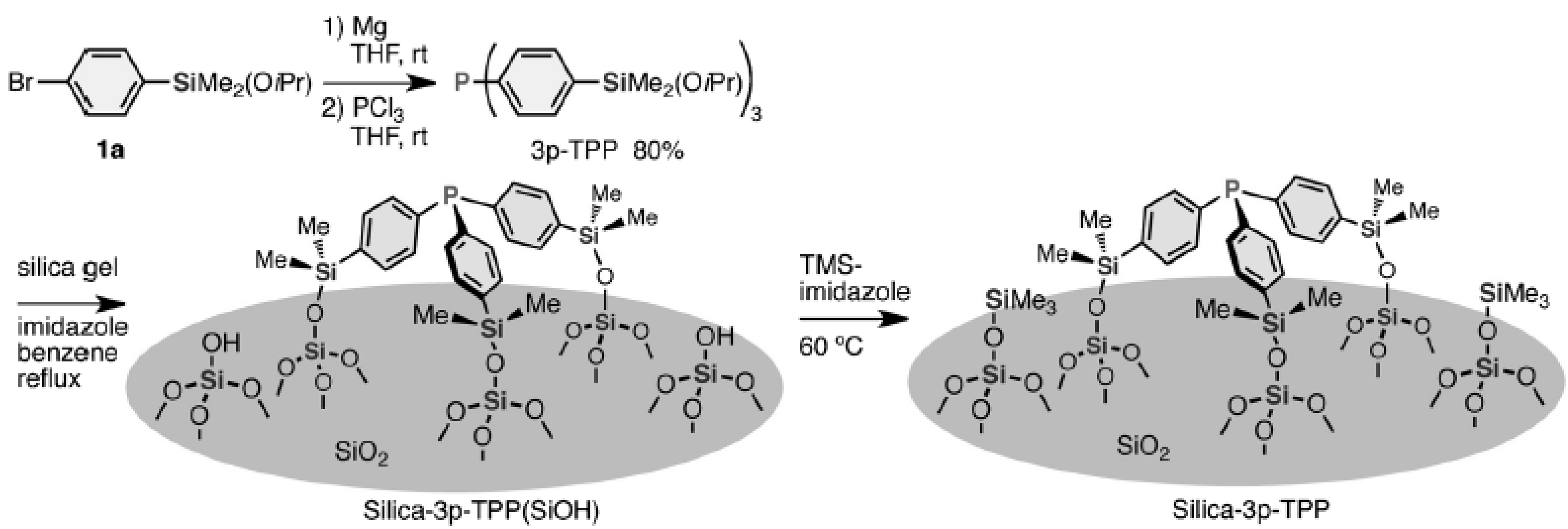


silica-SMAP

silica-3p-TPP

✓ easy preparation
✓ easy tuning

Synthesis of silica-3p-TPP[1]



0.20 mmol/g, TMS/TPP = 2:1

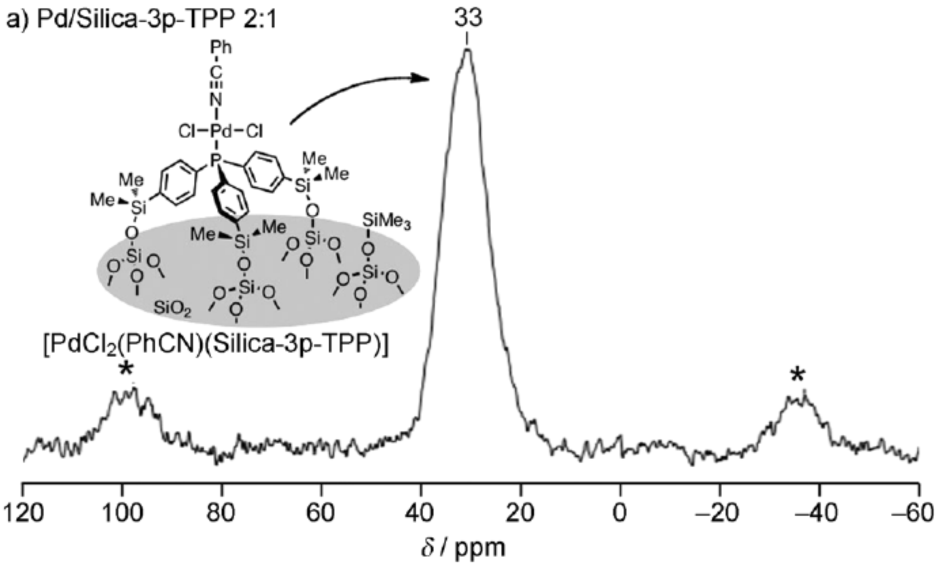
1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057

Silica-3p-TPP Also Forms Unsatureted Complex[1)]

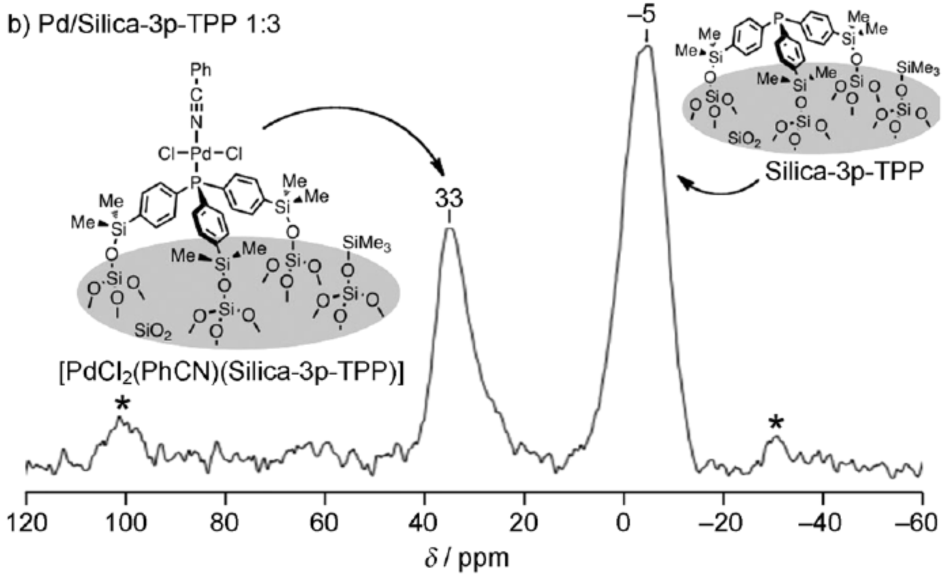
^{31}P CP/MAS NMR spectra

a) Pd/silica-3p-TPP = 2:1
b) Pd/silica-3p-TPP = 1:3
c) Pd/silica-1p-TPP = 1:3

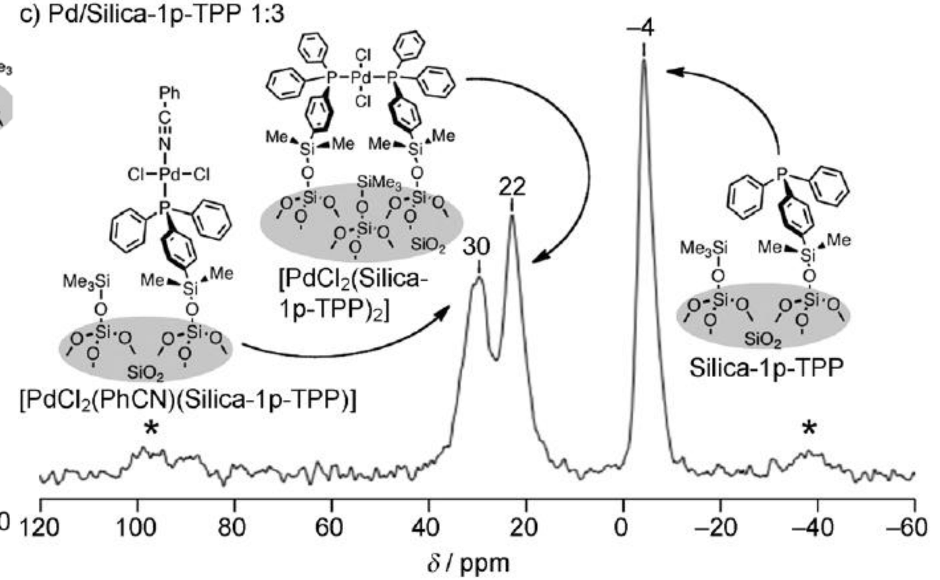
a)



b)

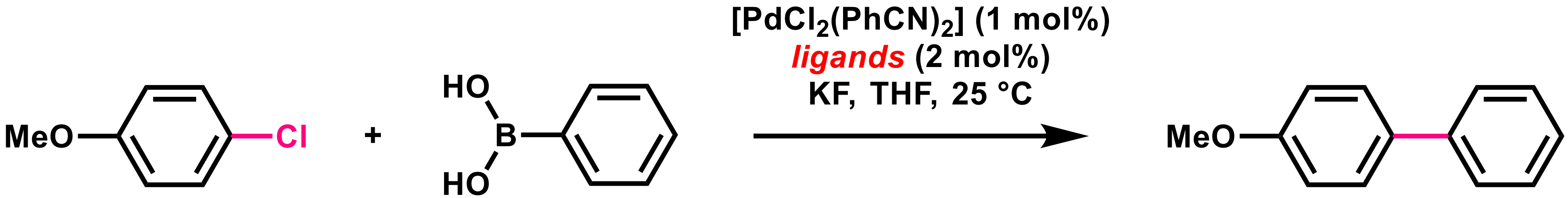


c)



1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057

Ligand Effect in Pd-catalyzed Suzuki Coupling[1)]



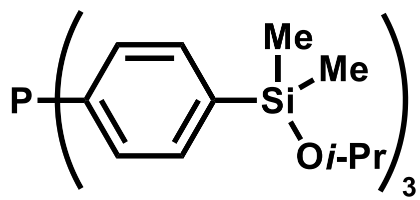
ligands

none

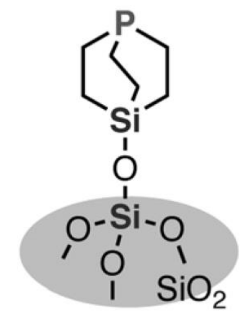
0%

PPh_3

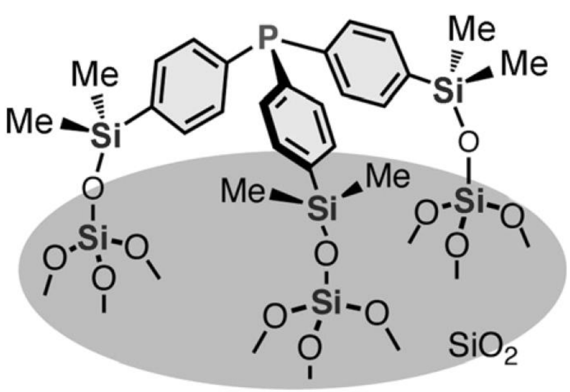
0%



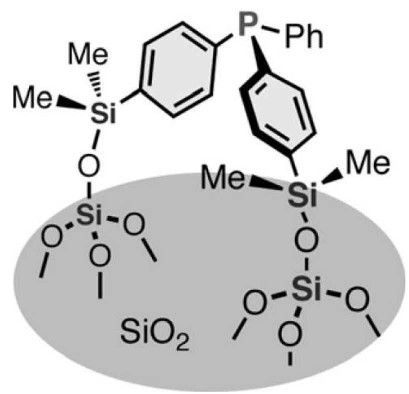
0%



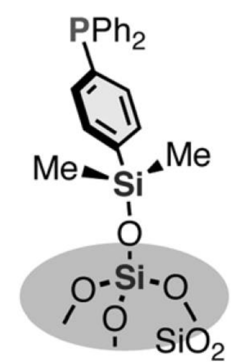
silica-SMAP
53%



silica-3p-TPP
97%



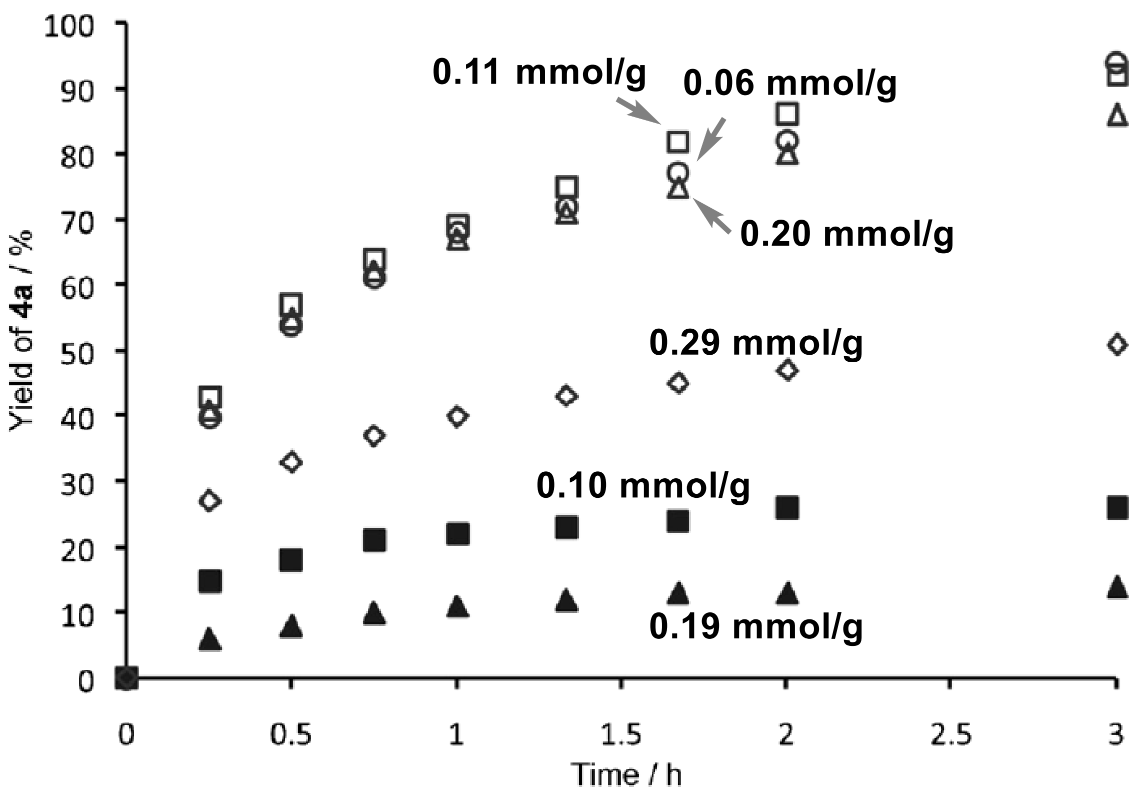
silica-2p-TPP
49%



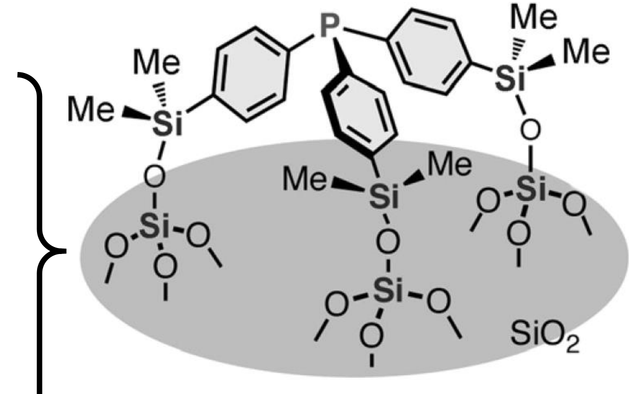
silica-1p-TPP
11%

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057

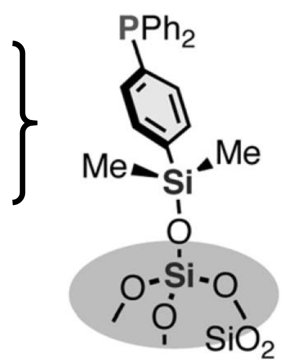
Effect of P-atom Density [1)]



time-yield profile



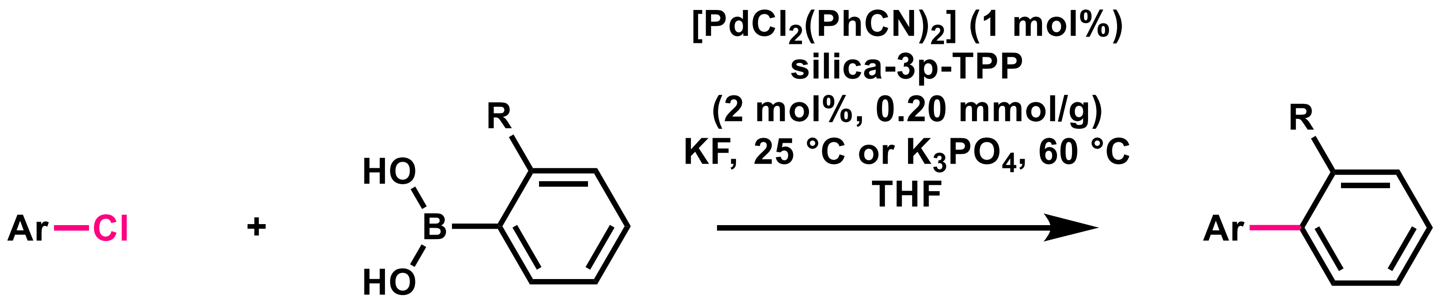
silica-3p-TPP

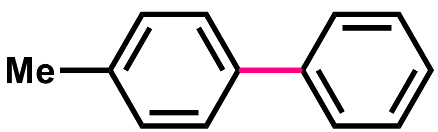


silica-1p-TPP

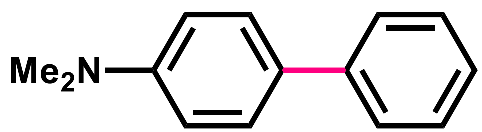
1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057

Substrate Scope[1)]

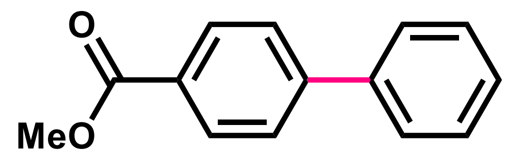




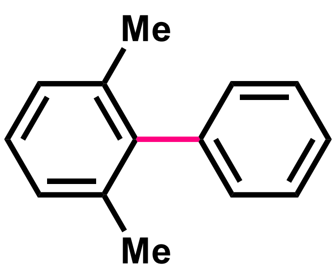
91% (25 °C)



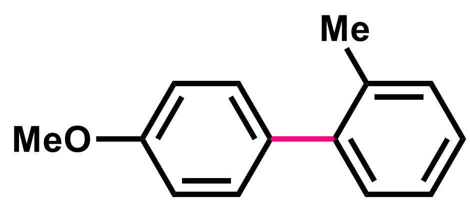
85% (25 °C)



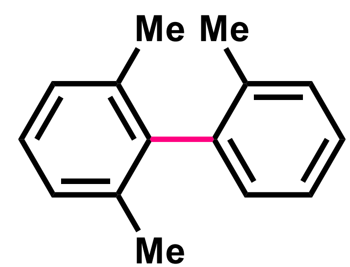
94% (25 °C)



85% (60 °C)



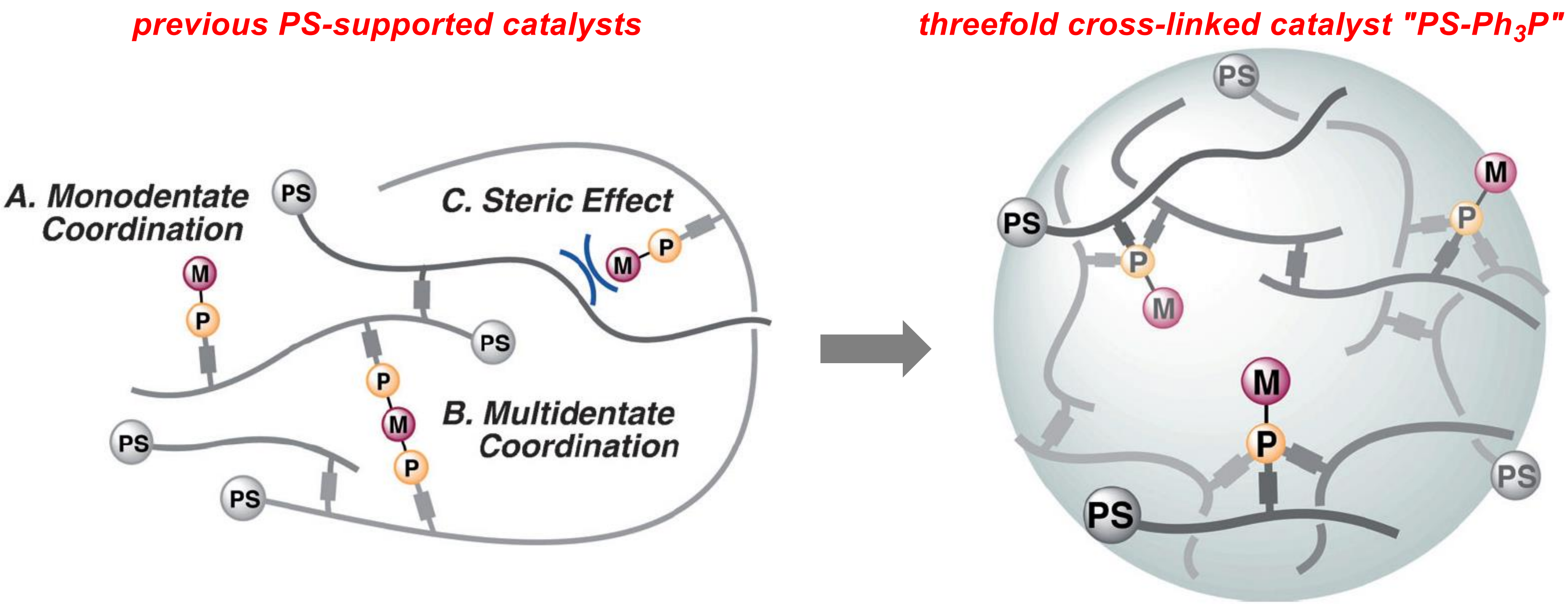
82% (60 °C)



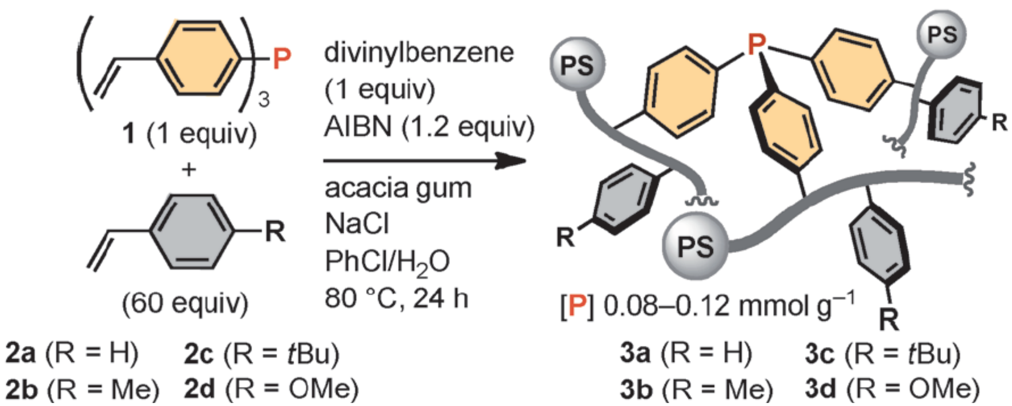
80% (60 °C)

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057

Polystyrene(PS)-supported catalyst "PS-Ph_3P"[1)]

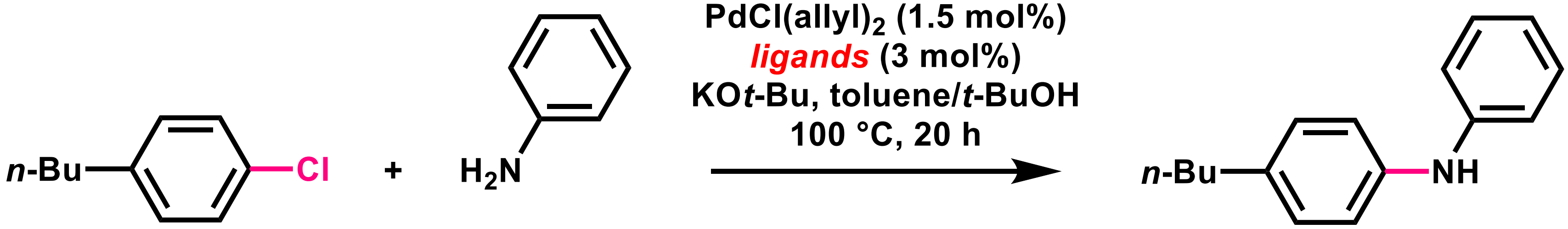


synthesis of "PS-Ph_3P"

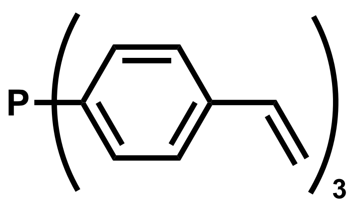


1. Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12322.

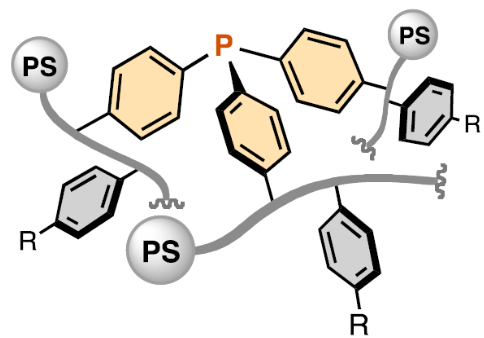
Hartwig-Buchwald Amination under Harsh Condition[1]



ligands

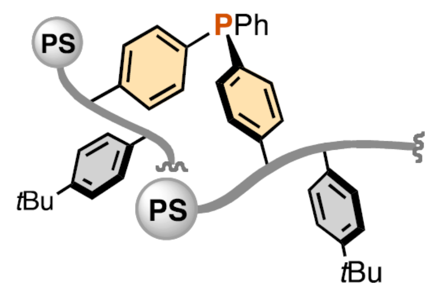


0%



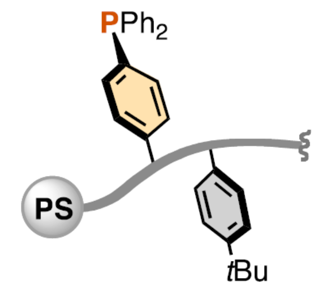
PS-Ph_3P (3fold)

R = H: 51%
R = OMe: 51%
R = Me: 92%
R = *t*-Bu: 99%



PS-Ph_3P (2fold, R = *t*-Bu)

52%



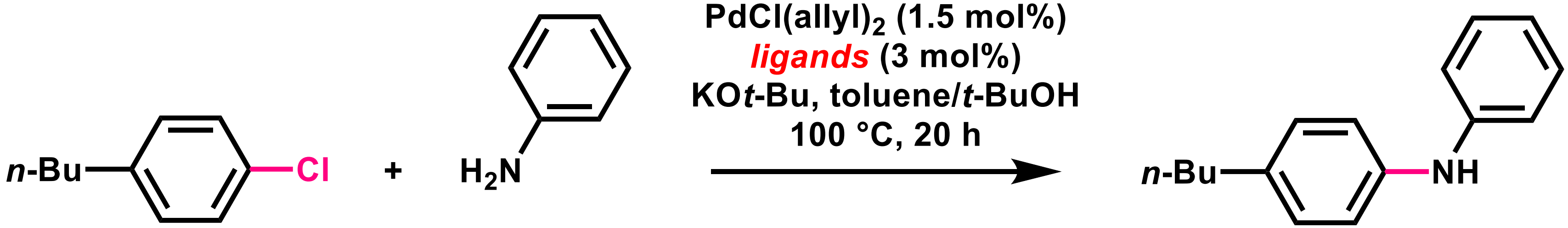
PS-Ph_3P (1fold, R = *t*-Bu)

6%

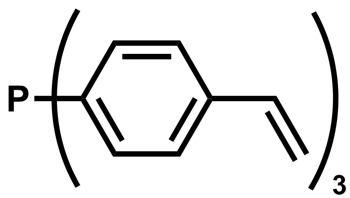
silica-SMAP
0% (decomp. of ligand)

1. Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12322.

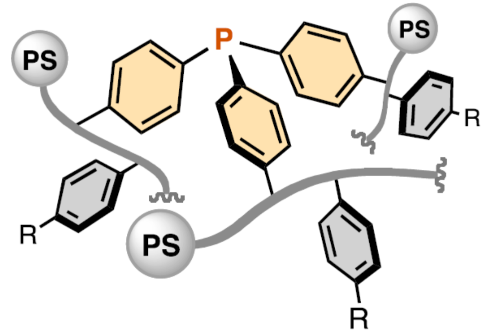
Hartwig-Buchwald Amination under Harsh Condition[1)]



ligands

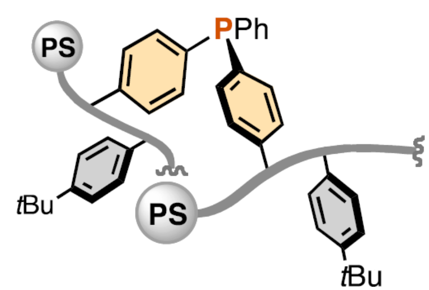


0%



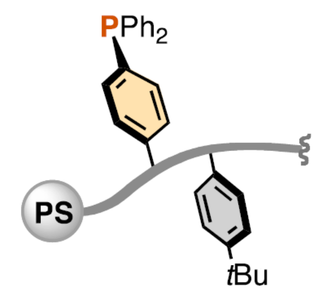
PS-Ph_3P (3fold)

R = H: 51%
R = OMe: 51%
R = Me: 92%
R = *t*-Bu: 99%



PS-Ph_3P (2fold, R = *t*-Bu)

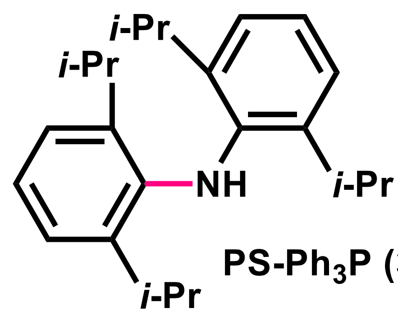
52%



PS-Ph_3P (1fold, R = *t*-Bu)

6%

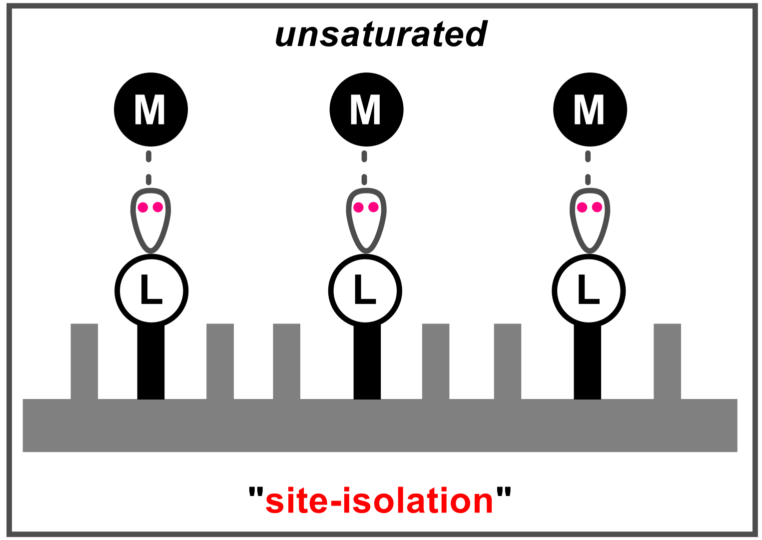
silica-SMAP
0% (decomp. of ligand)

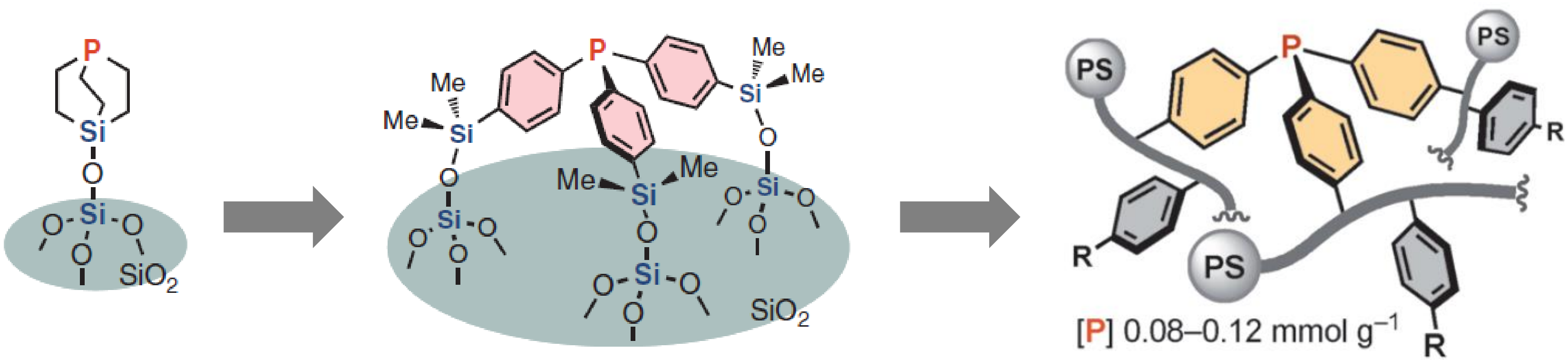


PS-Ph_3P (3fold, R =*t*-Bu)
80%

1. Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12322.

Short Summary





silica-SMAP

- ✓ air-stable
- ✓ electron-rich
- ✓ compact

silica-3p-TPP

- ✓ easy modification of ligand

PS-Ph_3P

- ✓ easy modification of solid support
- ✓ chemically stable

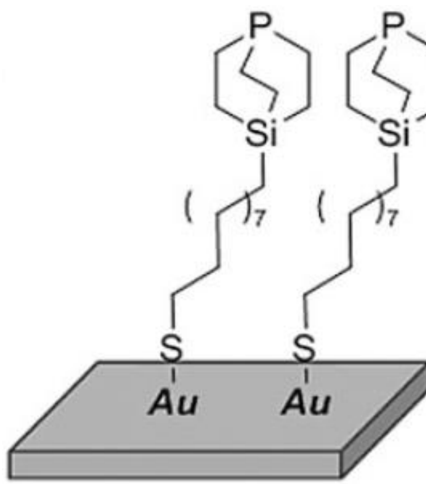
Contents

1. Introduction of solid-supported catalyst

2. Study 1; Site-isolation

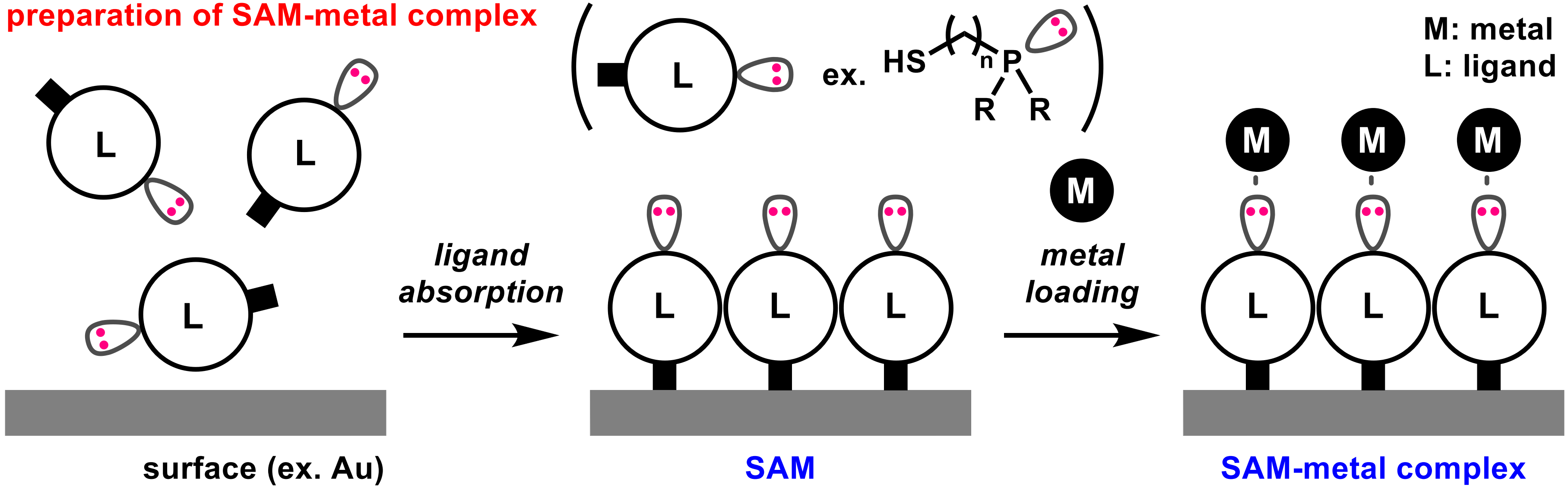
2.1 Silica-SMAP 2.2 Silica-3p-TPP 2.3 PS-Ph_3P

3. Study 2; Self-assembled monolayers



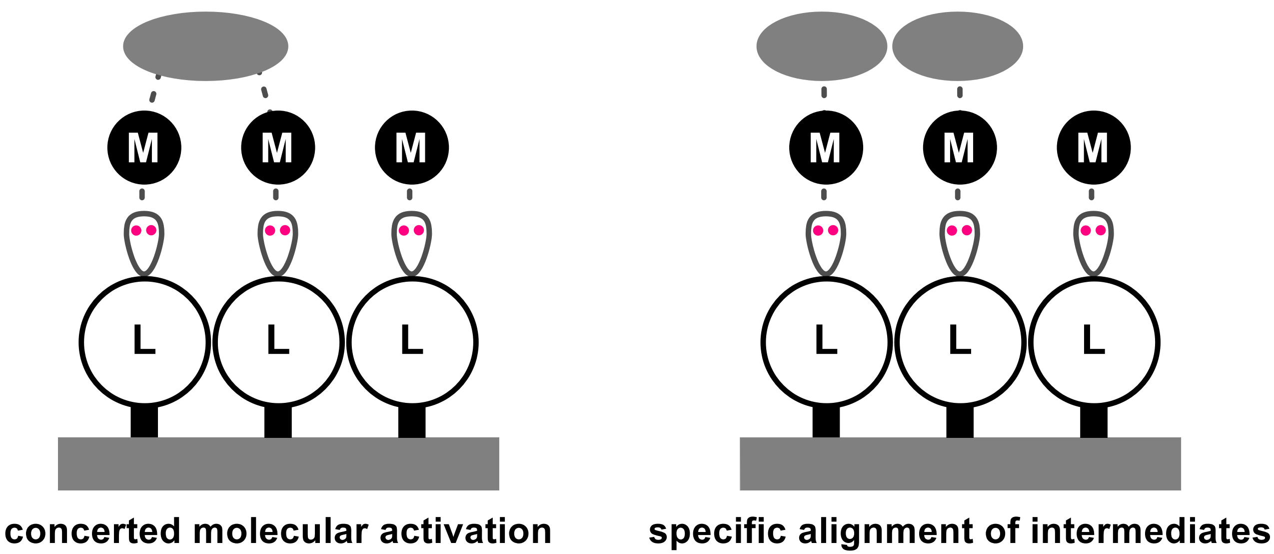
Catalysts Using Self-Assembled Monolayer (SAM)

preparation of SAM-metal complex



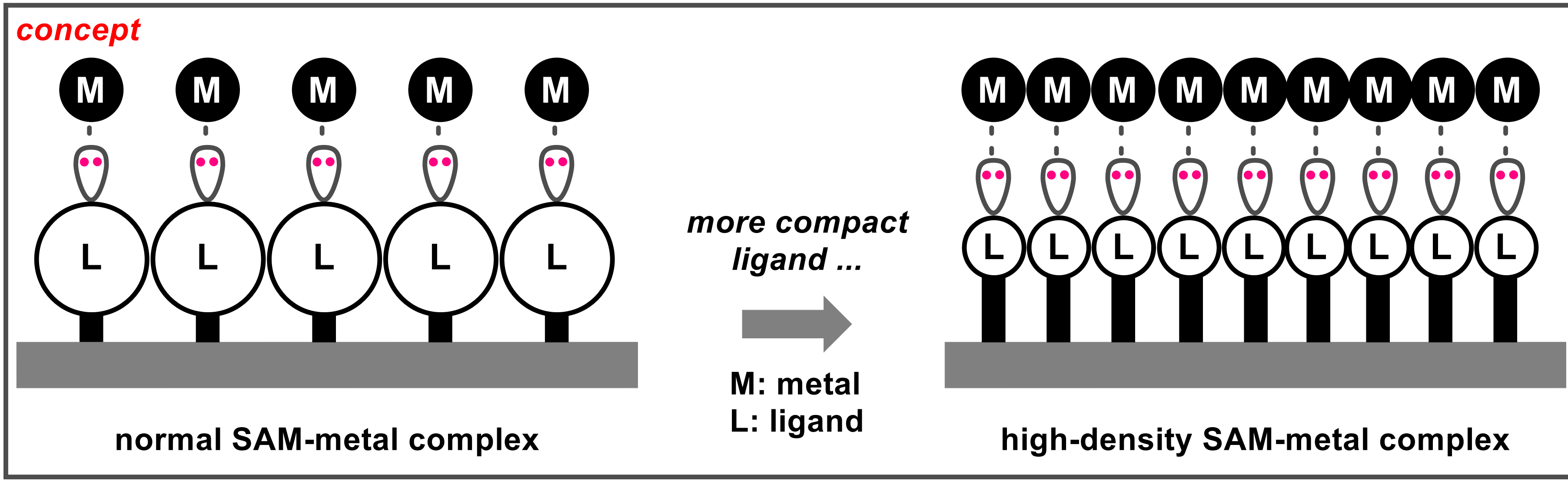
✓ easy preparation

synergistic effects by SAM-metal complex catalyst (協同効果)

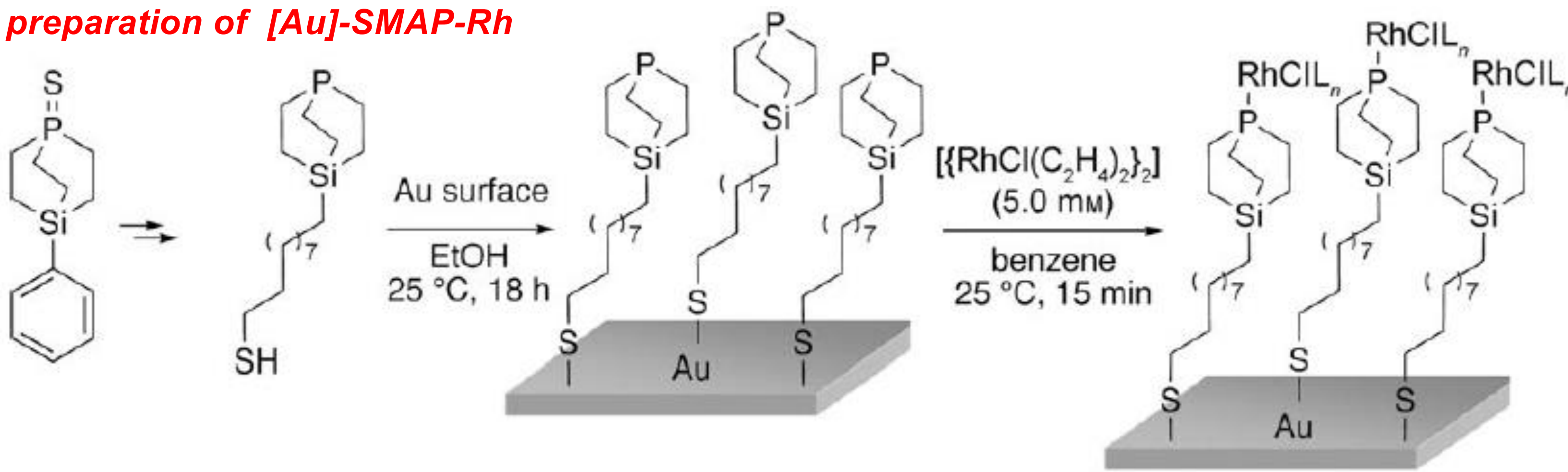


✓ unique activity
✓ unique selectivity

SMAP on High-density Self-assembled Monolayer (SAM)



preparation of [Au]-SMAP-Rh



[Au]-SMAP

S: 0.69 nmol/cm*

(cf. linear tholate: 0.75 nmol/cm*)

[Au]-SMAP-Rh

Rh: 0.71 ± 0.02 nmol/cm*

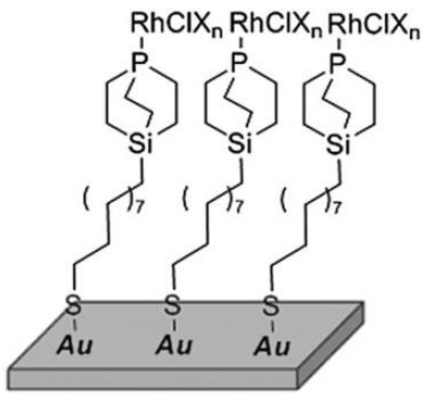
* determined by ICP-MS

1. Sawamura, M. *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 5627.

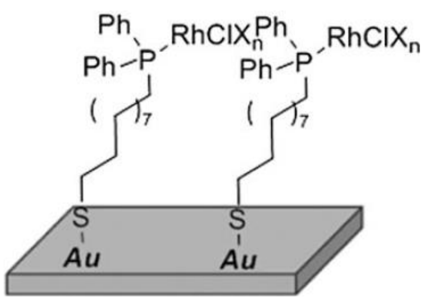
Dehydrogenative Silylation by [Au]-SMAP-Rh[1)]

$$\text{EtO–H} \xrightarrow[\text{hexane, 25 °C, 16 h}]{\text{Me}_2\text{PhSiH, } \textit{catalyst}} \text{EtO–SiPhMe}_2$$

catalyst	[Si]/[Rh]	yield	TON
$[RhCl(C_2H_4)_2]_2$	43000:1	36%	15000
$[RhCl(C_2H_4)_2]_2$:SMAP = 1:1	43000:1	9%	3900
[Au]-SMAP-Rh	**75000:1**	**80%**	**60000**
2nd run	75000:1	81%	61000
3rd run	75000:1	78%	59000
4th run	75000:1	73%	55000
[Au]-Ph_2P-Rh	67000:1	45%	30000
2nd run	67000:1	7%	4700



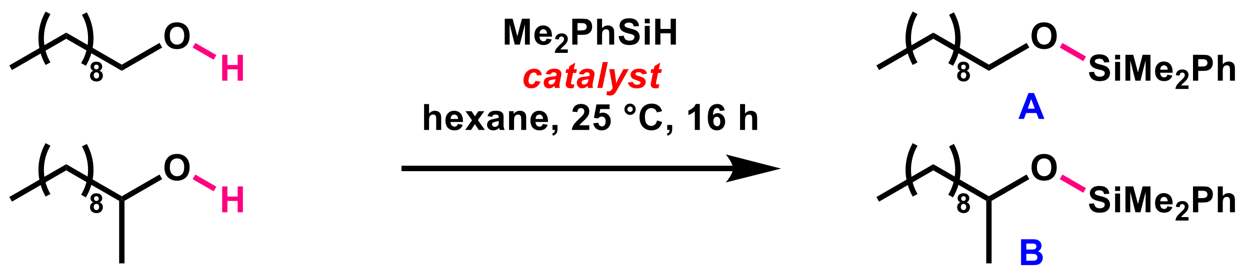
[Au]-SMAP-Rh



[Au]-Ph_2P-Rh
(X = ethylene)

1. Sawamura, M. *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 5627.

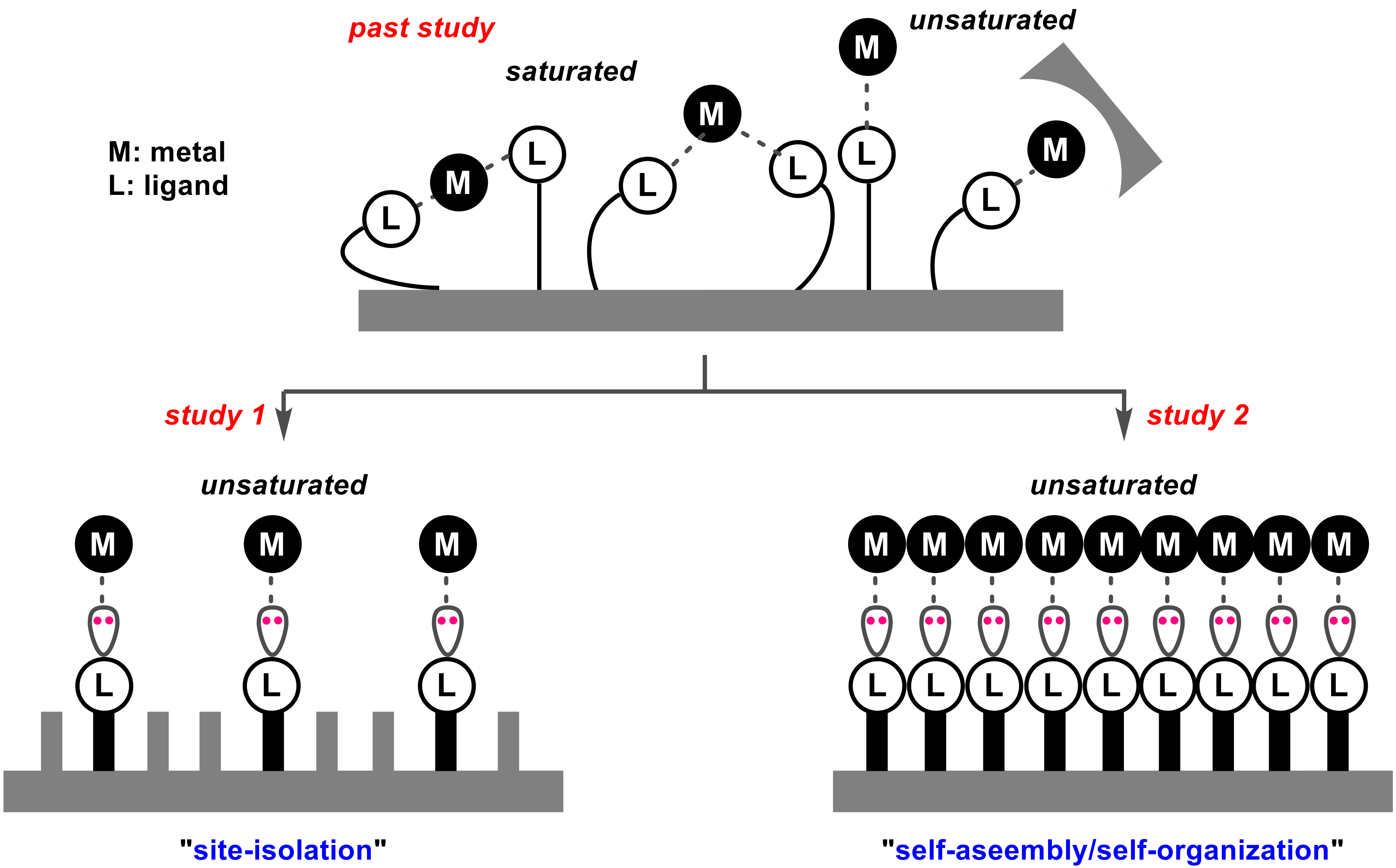
Prim-alchohol-selective Dehydrogenative Silylation[1)]



catalysts	[Si]/[Rh]	yield	TON	A/B
$[RhCl(C_2H_4)_2]_2$	86000:1	7%	6000	71:29
$[RhCl(C_2H_4)_2]_2$:SMAP = 1:1	86000:1	3%	2600	72:28
DTBM-xantphos-[Cu]	50:1	92%	46	98:2
[Au]-SMAP-Rh	150000:1	60%	90000	>99.5:0.5
2nd run	150000:1	58%	87000	>99.5:0.5
3rd run	150000:1	55%	83000	>99.5:0.5
4th run	150000:1	50%	75000	>99.5:0.5
[Au]-Ph_2P-Rh	150000:1	43%	58000	81:19

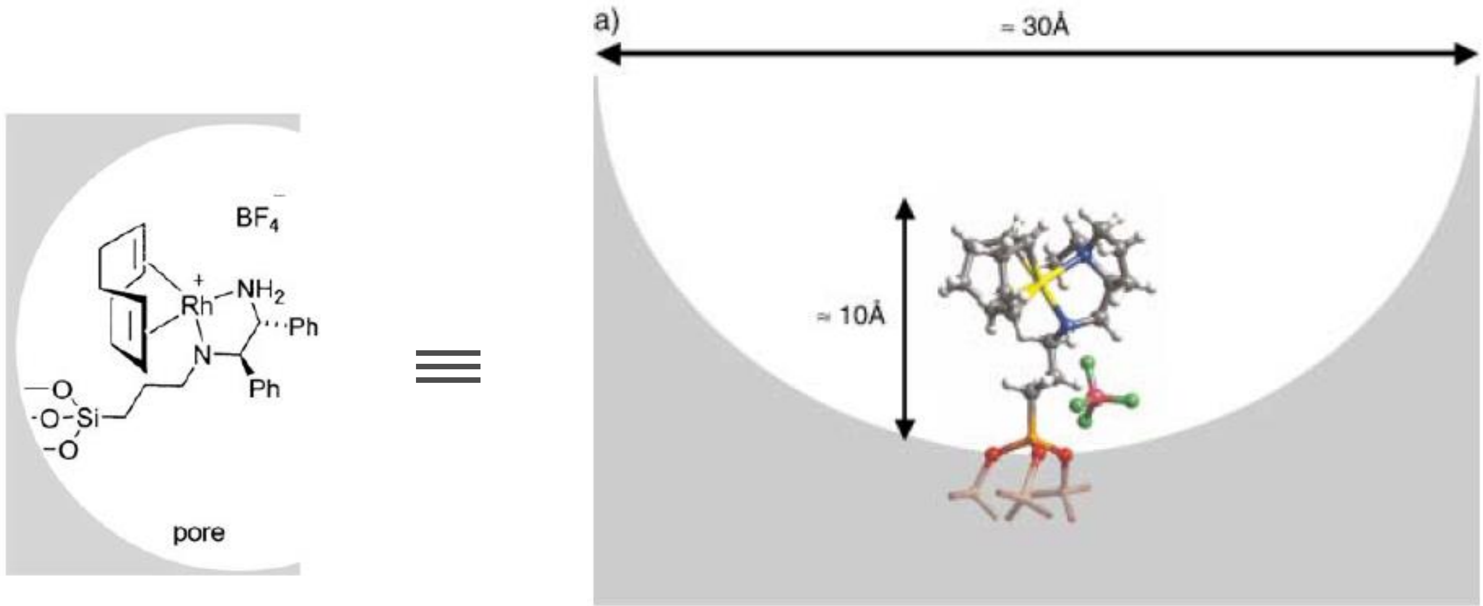
1. Sawamura, M. *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 5627.
2. Ito, H.; Watanabe, A.; Sawamura, M. *Org. Lett.* **2005**, *7*, 1869.

Summary


M: metal
L: ligand
past study
saturated
unsaturated
study 1
study 2
unsaturated
unsaturated
"site-isolation"
"self-aseembly/self-organization"

Appendix

Graphical Model[1)]



1. Jones, M. D.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Vaughen, D. E. W.; *Angew. Chem. Int. Ed.* **2003**, *42*, 4326.

Electronic Nature of Various Phosphines[1)]

Table 1. V_{min} (kcal/mol) for various phosphines and $^1J(^{31}P, ^{77}Se)$ (Hz) for phosphine selenides

Entry	SMAP	R_3P	V_{mim} kcal mol^{-1}	$^1J(^{31}P,^{77}Se)$ /Hz
1	4-Me_2N-Ph-SMAP (**1b**)		−46.58	729.3
2		(t-Bu)$_3$P	−45.48[a]	n.d.
3		(i-Pr)$_3$P	−44.47[a]	n.d.
4	4-MeO-Ph-SMAP (**1c**)		−44.30	734.2
5	4-Me-Ph-SMAP (**1d**)		−43.86	733.0
6		Bu_3P	−43.71[a]	717.1
7	Ph-SMAP (**1a**)		−43.14	735.4
8		Me_3P	−43.02[a]	713.5
9	4-Cl-Ph-SMAP (**1e**)		−40.86	738.5
10		Me_2PhP	−40.41[a]	n.d.
11	4-CF_3-Ph-SMAP (**1f**)		−39.85	739.1
12	3,5-(CF_3)$_2$-Ph-SMAP (**1g**)		−37.77	742.2
13		$MePh_2P$	Š36.76[a]	n.d.

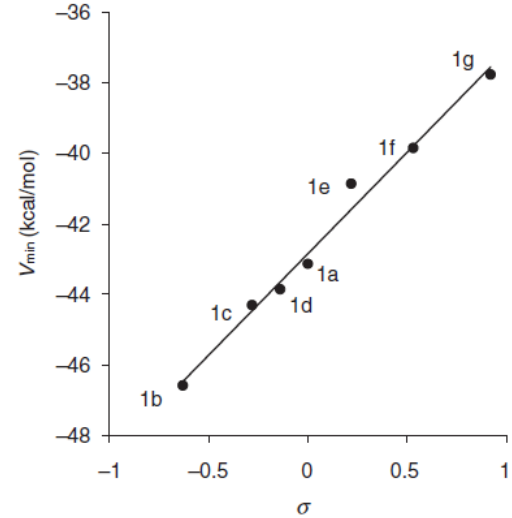


Figure 2. A plot of V_{min} (kcal/mol) vs Hammett's substituent constants σ's for SMAP derivatives **1a**–**1g**. A value two-fold greater than the σ value of m-CF_3 was used for **1g**.

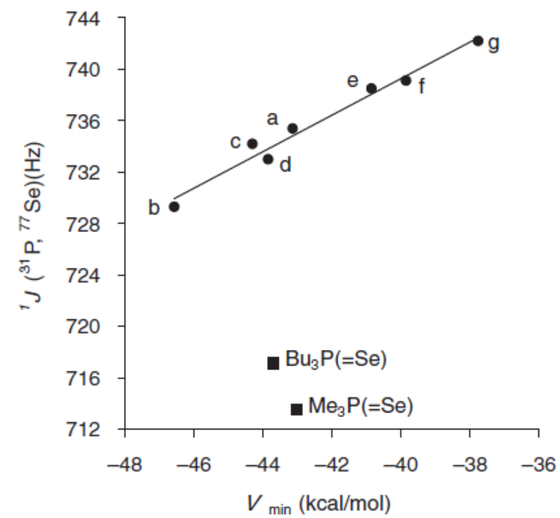


Figure 3. A plot of $^1J(^{31}P,^{77}Se)$ vs V_{min} of the phosphine derivatives. The correlation line is associated with **1a**–**1g**/**4a**–**4g**.

1. Ochida, A.; Ito, S.; Miyahara, T.; Ito, H.; Sawamura, M. *Chem. Lett.* **2006**, *35*, 294.

^{31}P CP/MAS NMR Spectra of Silica-3p-TPP-(SiOH)[1]

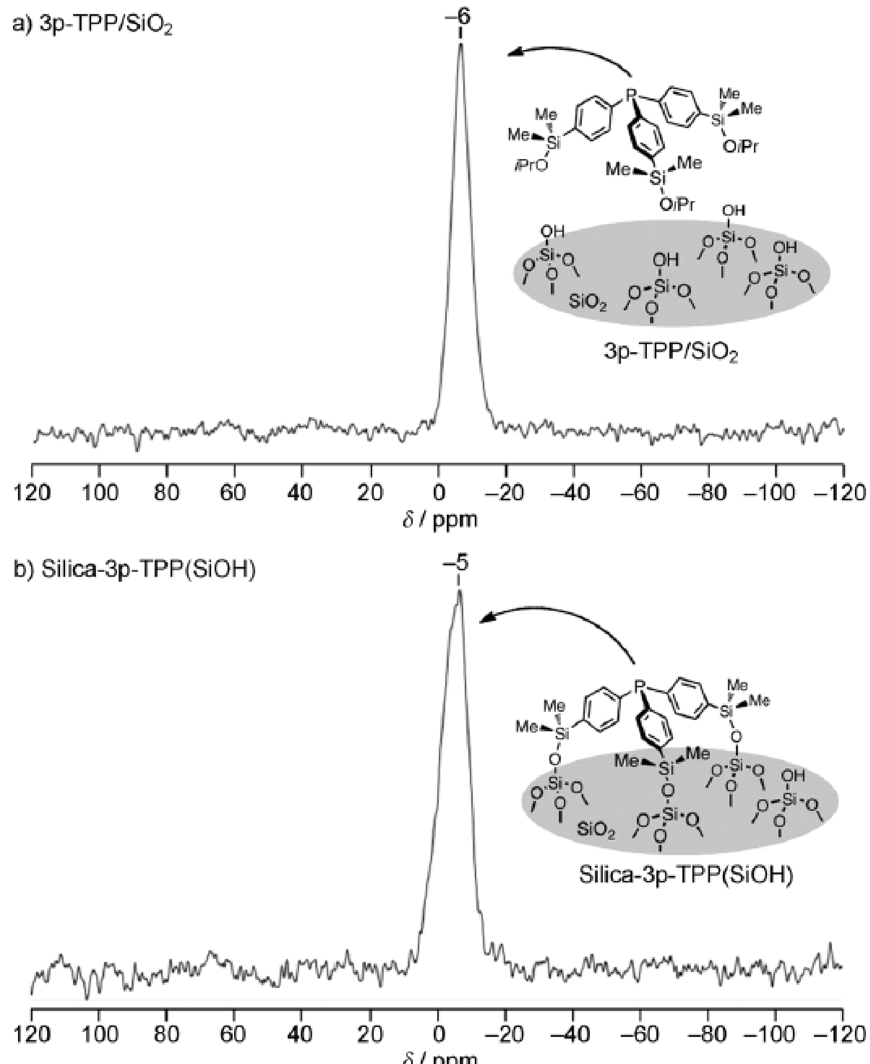


Figure 2. ^{31}P CP/MAS NMR spectra of a) 3p-TPP/SiO_2 and b) Silica-3p-TPP-(SiOH).

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

^{29}Si CP/MAS NMR Spectra of Silica-3p-TPP-(SiOH)[1)]

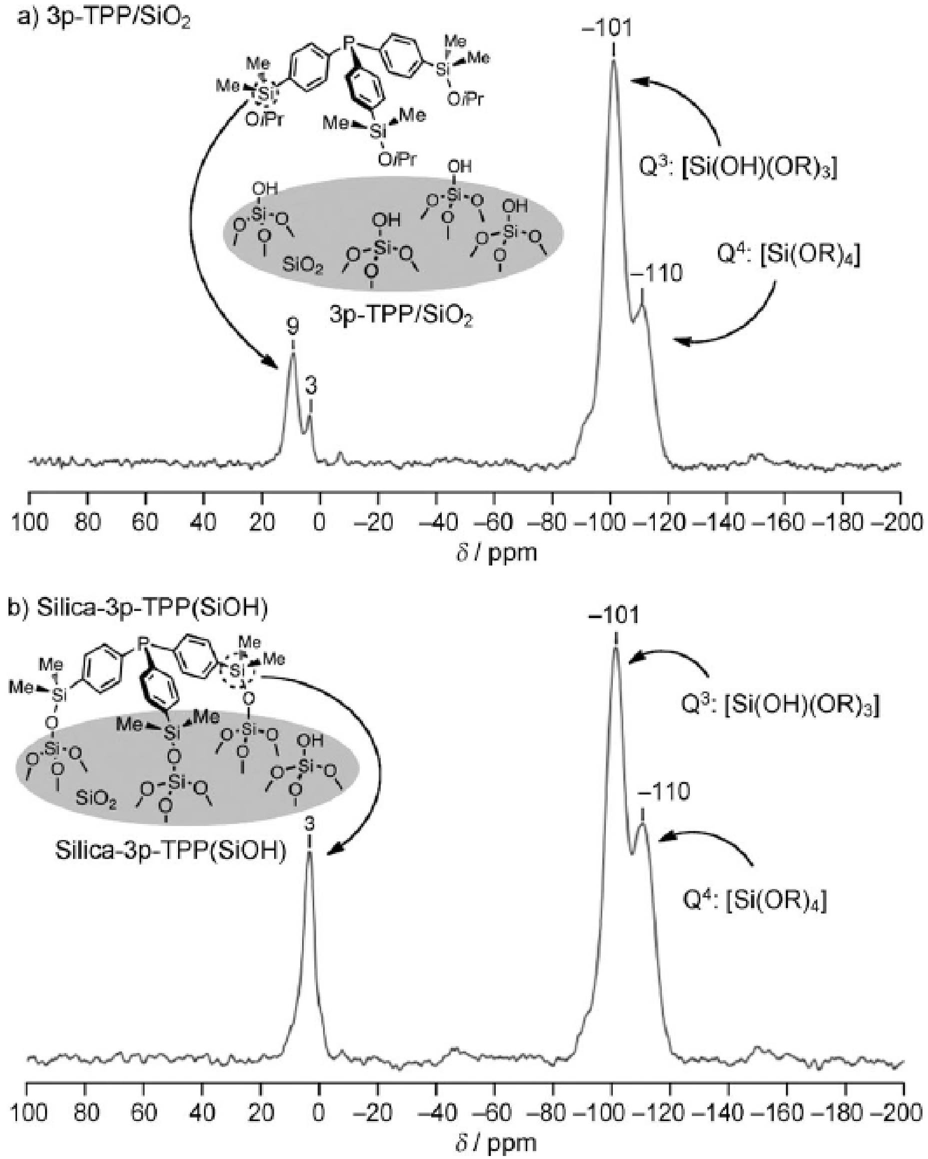


Figure 3. ^{29}Si CP/MAS NMR spectra of a) 3p-TPP/SiO_2 and b) Silica-3p-TPP(SiOH).

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

^{13}C CP/MAS NMR Spectra of Silica-3p-TPP-(SiOH)[1)]

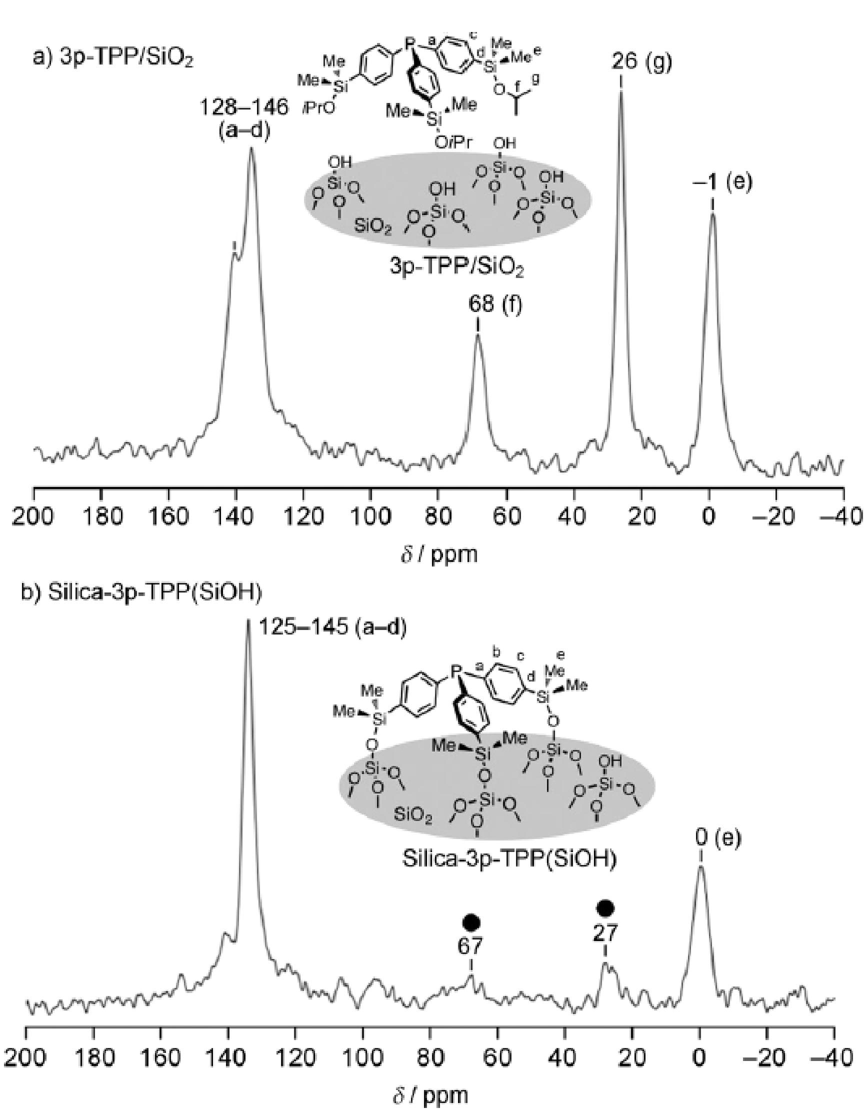
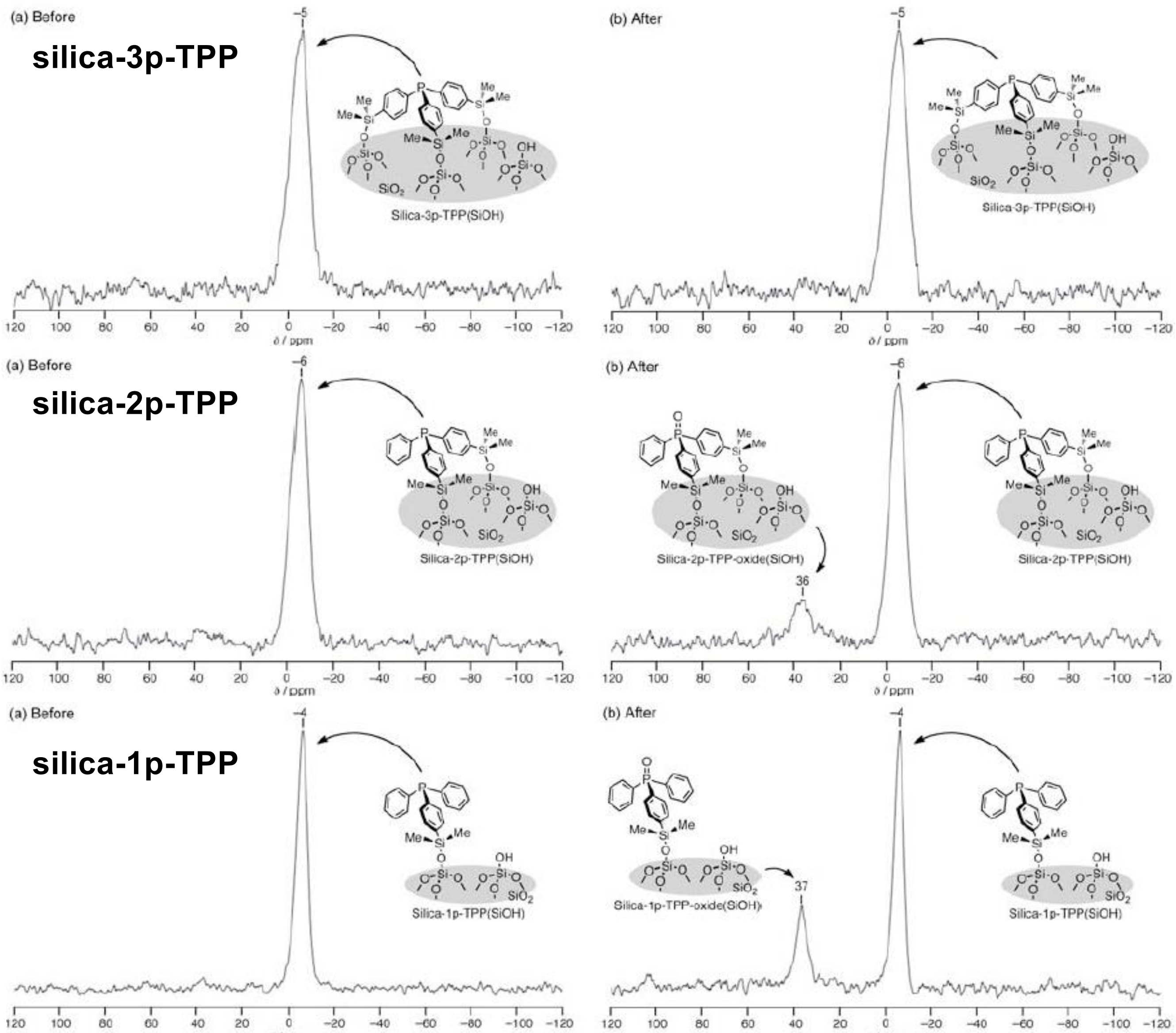


Figure 4. ^{13}C CP/MAS NMR spectra of a) 3p-TPP/SiO_2 and b) Silica-3p-TPP(SiOH). Isopropoxy groups derived from 3p-TPP (●).

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

Air-stability of Silica-3p-TPP [1)]



Silica-3/2/1/p -TPP was heated in benzene under air at 100 °C for 10 h.

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

^{31}P NMR spectra of 3p-TPP and Pd Catalyst[1)]

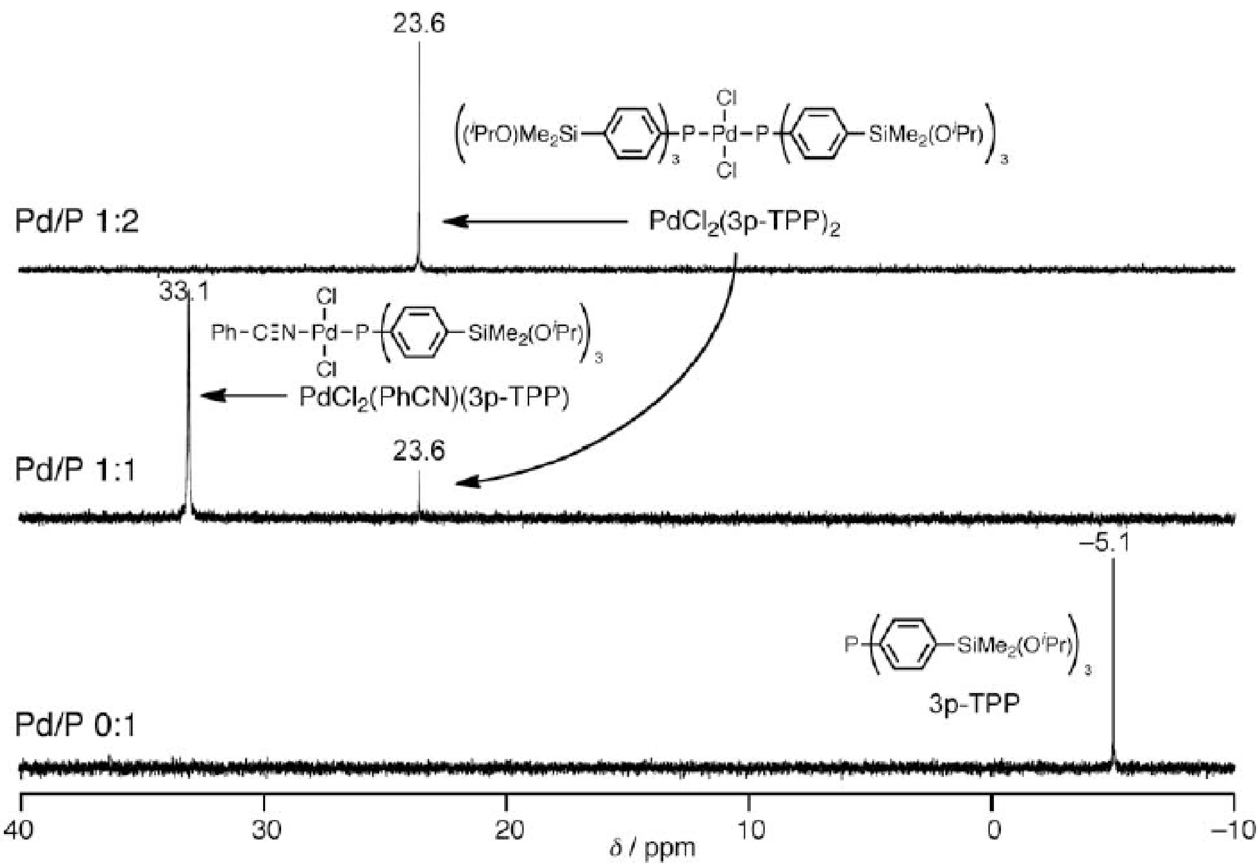


Figure S14. ^{31}P NMR spectra ($CDCl_3$) in the reactions of 3p-TPP and [$PdCl_2(PhCN)_2$].

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

31P NMR spectra of 1p-TPP and Pd Catalyst[1)]

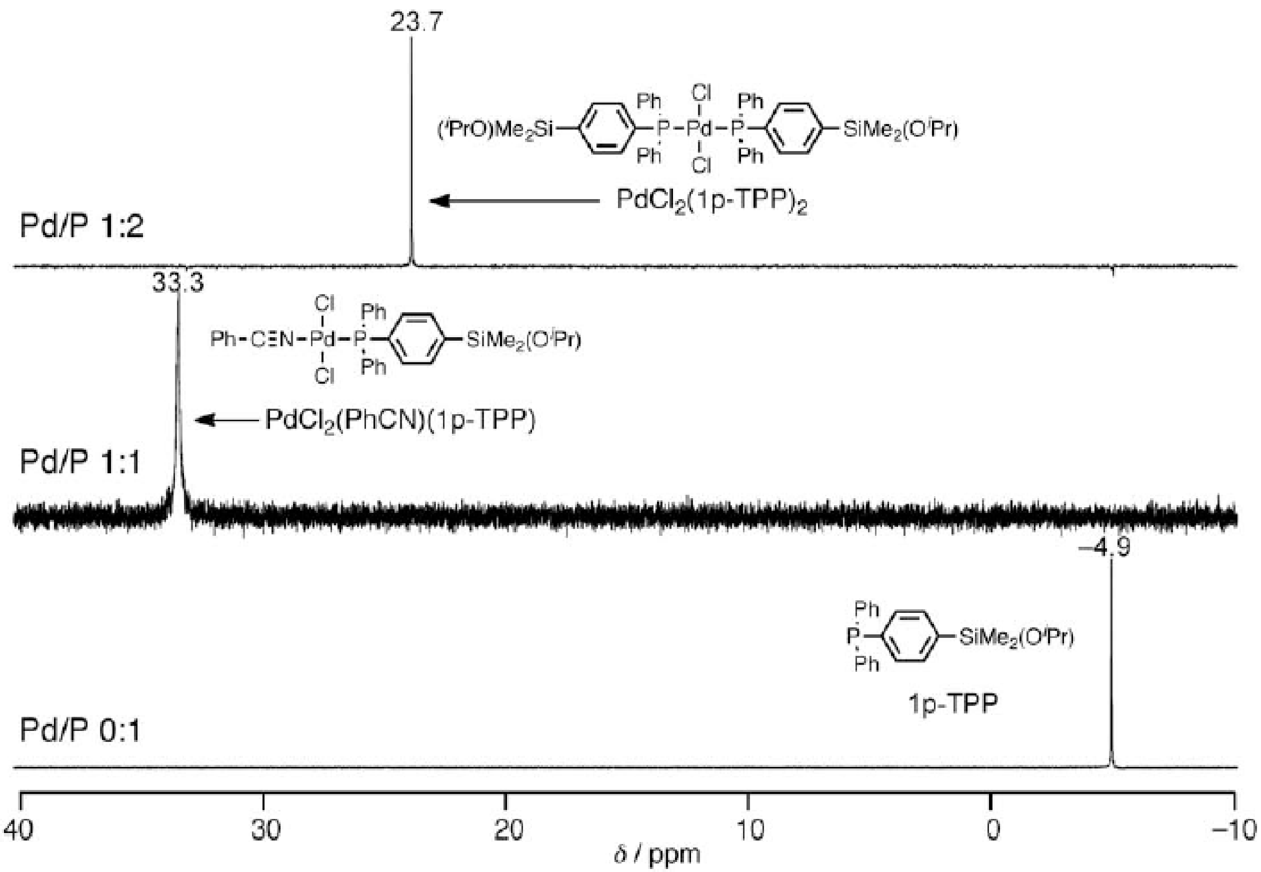
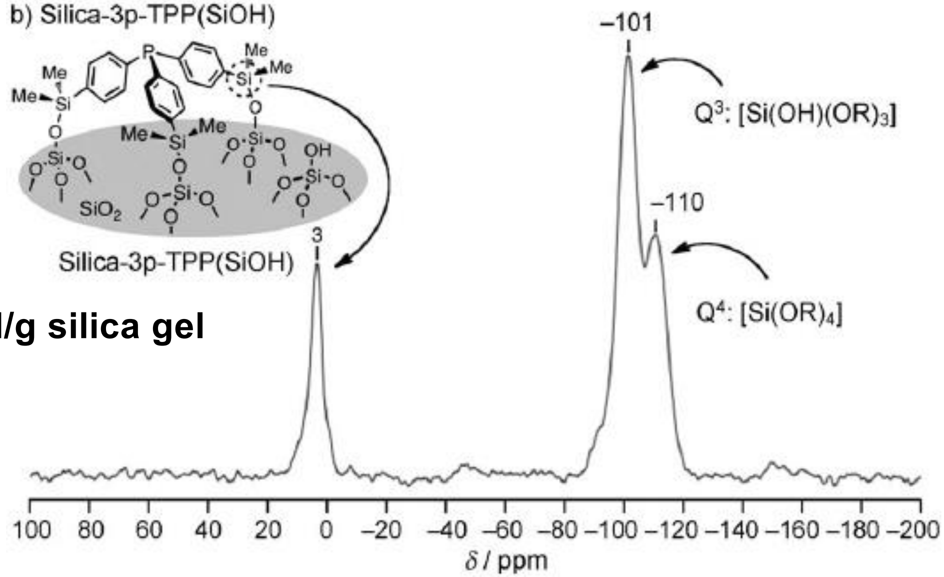


Figure S15. ^{31}P NMR spectra ($CDCl_3$) in the reactions of 1p-TPP and [$PdCl_2(PhCN)_2$].

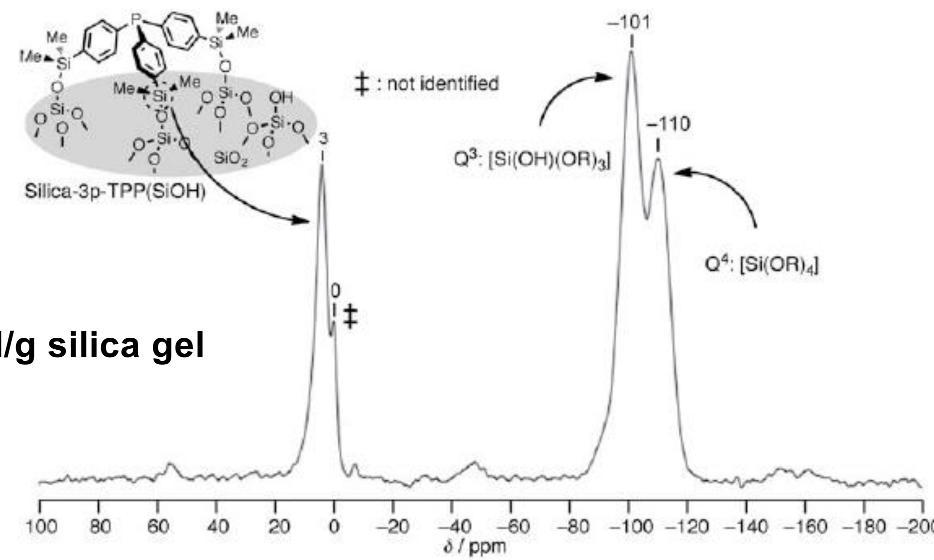
1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

Over-modification of Silica Surface[1)]

0.20 mmol/g silica gel



0.29 mmol/g silica gel



^{31}P CP/MAS NMR of silica-3p-TPP(SiOH)

1. Iwai, T.; Tanaka, R.; Harada, T.; Sawamura, M. *Chem. Eur. J.* **2014**, *20*, 1057.

PS-Ph$_3$P Also Forms Unsaturated Complex[1)]

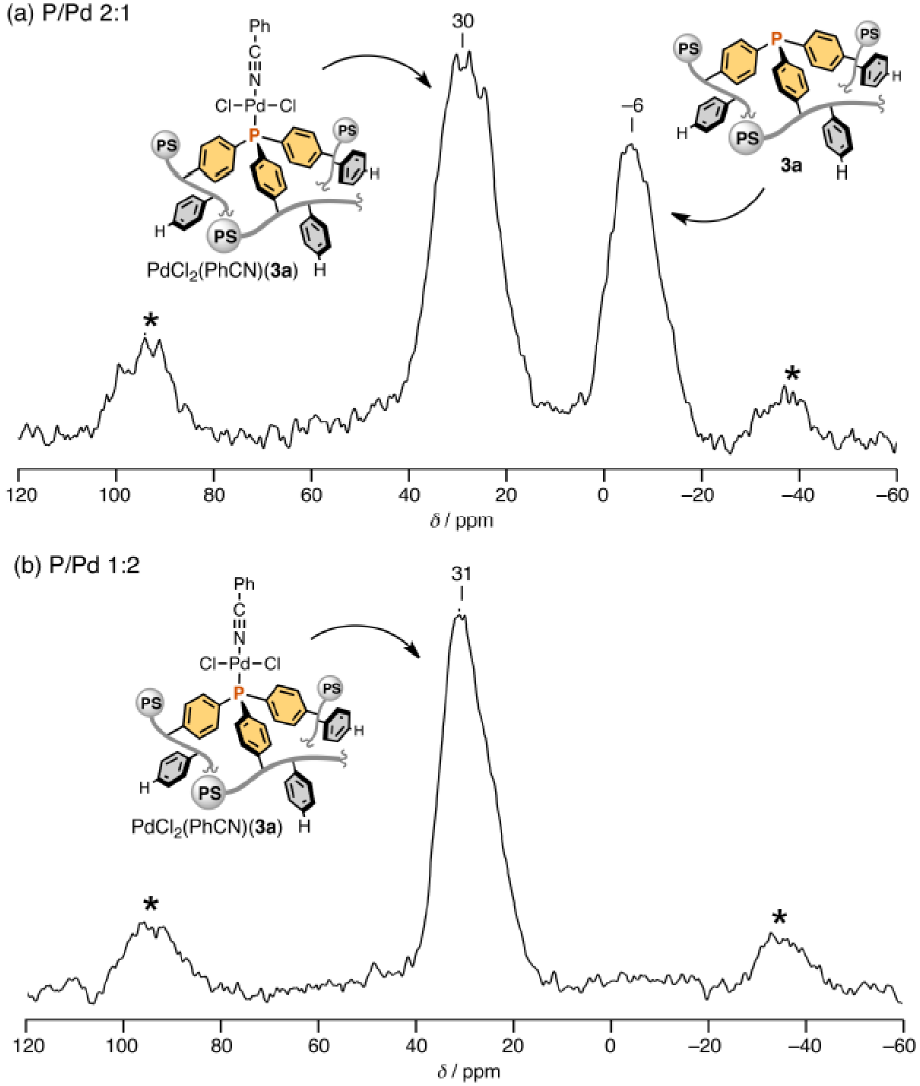


Figure S9. ^{31}P CP/MAS NMR spectra obtained after the reaction of **3a** and [PdCl$_2$(PhCN)$_2$] (P/Pd (a) 2:1 and (b) 1:2). Asterisks(*) indicate spinning side bands.

1. Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12322.

1-Fold PS-Ph_3P Can Form Saturated Complex[1)]

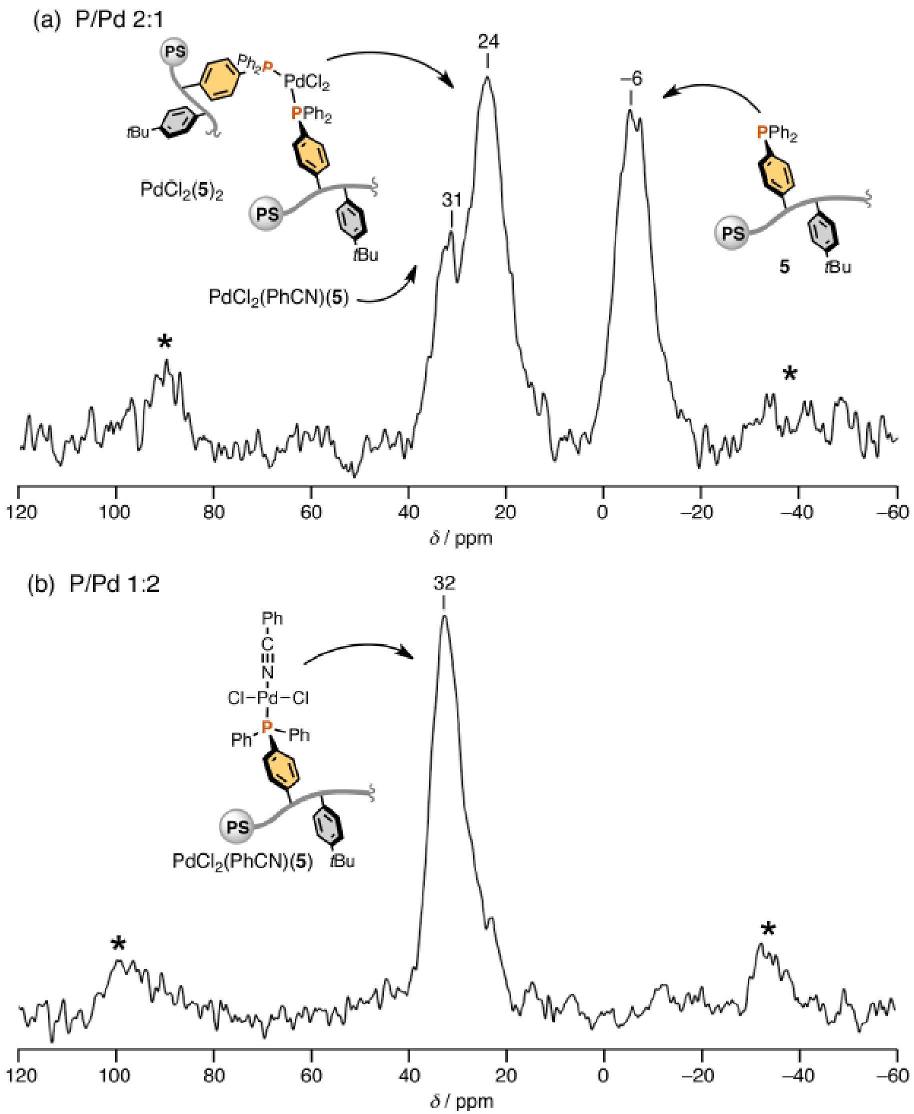


Figure S14. ^{31}P CP/MAS NMR spectrum obtained after the reaction of **5** and $[PdCl_2(PhCN)_2]$ (P/Pd (a) 2:1 and (b) 1:2). Asterisks(*) indicate spinning side bands.

1. Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 12322.