Supporting Informations

Phosphine-Dendrimer Stabilized Palladium Nanoparticles, a Highly Active and Recyclable Catalyst for Suzuki-Miyaura Reaction and Hydrogenation

Lei Wu,^{a, b} Bao-Lin Li,^{a, b} Yi-Yong Huang,^{a, b} Hai-Feng Zhou,^a Yan-Mei He,^a Qing-Hua Fan^{a, *}

^a *Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China;*

^b *Graduate School of the Chinese Academy of Sciences, Beijing 100080, China.*

fanqh@iccas.ac.cn

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1. General Information

Unless otherwise stated, all starting materials were obtained from commercial supplies and used as received. Anhydrous solvents were obtained as follow: THF, dioxane and toluene by distillation from sodium and benzophenone (Few amounts of thiophene in toluene was firstly removed by using concentrated H_2SO_4); dichloromethane from CaH_2 . All moisture and air sensitive reactions were carried out in a flame dried flask under nitrogen atmosphere. Column chromatography was performed with silica gel 200~300 mesh. All ^1H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-DMX 300 for a CDCl_3 solution in the presence of tetramethylsilane as an internal standard and reported in ppm (δ). ^{31}P NMR (121 MHz) were measured on a Bruker-DMX 400 and referenced to an external sample (85% H_3PO_4). Mass spectra measurements were carried out with a Finnigan model Mat SSQ-710 instrument. MALDI-TOF mass spectra were recorded on a BIFLEX_ instrument with α -cyano-4-hydroxycinnamic acid (CCA) as the matrix. Element analysis was carried out on a Flash EA 112 instrument. Transmission electron microscopy (TEM): the chloroform dispersion of catalyst was drop-cast onto a 300 mesh carbon coated copper grid, and TEM pictures were taken on a Hitachi H600 microscopy at an accelerating voltage of 75 kv.

2. Experiment Details

(1) Typical procedure for the synthesis of G_nDenP ($n = 1\sim3$):

25 mL two-necks flask was charged with 5 mL 0.5 M KPh₂ and cooled to -78°C. A solution of G_nCH₂Br (0.880 g, 0.5 mmol, n=3) in dried and degassed THF was added dropwisely with vigorous stirring. After 3 h, the mixture was allowed to stir at room temperature for 10 h. Most of the solvent was removed under reduced pressure. Then 30 mL MeOH was added to precipitate the crude product, which was further purified by flash chromatograph on silica gel (CH₂Cl₂/petroleum ether, 2:1), affording the dendritic phosphine ligands with 80~90% yields.

G₁DenP: white solid, m.p.: 100-102°C; ¹H NMR (300 MHz, CDCl₃) δ 3.30 (s, 2H), 4.80 (s, 4H), 6.25 (s, 2H), 6.35 (s, 1H), 7.27-7.38 (m, 20H); ¹³C NMR (75 MHz, CDCl₃) δ 36.31, 69.94, 100.34, 108.40, 108.49, 127.55, 127.93, 128.38, 128.46, 128.56, 128.76, 132.89, 133.14, 137.03, 159.76; ³¹P NMR (121 MHz, CH₂Cl₂) δ -10.30. MALDI- TOF MS: m/z 489.4 ([M+H]⁺).

G₂DenP: white solid, m.p.: 112-114°C; ¹H NMR (300 MHz, CDCl₃) δ 3.30 (s, 2H), 4.74 (s, 4H), 4.97 (s, 8H), 6.23 (s, 2H), 6.38 (s, 1H), 6.51-6.58 (m, 6H), 7.3-7.44 (m, 30H); ¹³C NMR (75 MHz, CDCl₃) δ 36.48, 68.01, 69.80, 70.13, 100.29, 101.55, 106.37, 108.39, 108.47, 127.59, 128.03, 128.25, 128.37, 128.46, 128.62, 128.79, 132.87, 133.11, 136.83, 139.44, 139.61, 159.62, 160.15; ³¹P NMR (121 MHz, CH₂Cl₂) δ -10.32. MALDI- TOF MS: m/z 913.4 ([M+H]⁺).

G₃DenP: white solid, m.p.: 124-126°C; ¹H NMR (300 MHz, CDCl₃) δ 3.32 (s, 2H), 4.77 (s, 2H), 4.93 (s, 8H), 4.99 (s, 16H), 6.27 (s, 2H), 6.39 (s, 1H), 6.51-6.67 (m, 18H), 7.28-7.39 (m, 50H); ¹³C NMR (75 MHz, CDCl₃) δ 36.39, 69.77, 69.98, 70.08, 100.26, 101.53, 101.61, 106.38, 108.38, 108.47, 127.54, 127.97, 128.34, 128.43, 128.56, 128.76, 132.83, 133.07, 136.77, 137.92, 138.11, 139.24, 139.40, 139.59, 159.63, 160.02, 160.16; ³¹P NMR (121 MHz, CH₂Cl₂) δ -10.32. MS(APCI): m/z 1763.0 ([M+H]⁺); MALDI-TOF MS: m/z 1762.0 ([M+H]⁺). Ana. Calcd. for C₁₁₇H₁₀₁O₁₄P: C, 79.75; H, 5.78. Found: C, 79.52; H, 5.86.

(2) TEM images and diameter distribution of G_nDenP-Pd:

G₁DenP-Pd

5.0 nm ± 0.4 nm

G₂DenP-Pd

4.6 nm ± 0.5 nm

G₃DenP-Pd

3.2 nm ± 0.5 nm

(3) General procedure for the Suzuki coupling reactions and catalyst recycling:

To a 25 mL flask was added aryl halides (1.25 mmol), arylboronic acid (1.875 mmol), 676 mg $K_3PO_4 \cdot 7H_2O$, 0.06 mol% **G_nDenP**-Pd (1.5 mg, n=2) and 10 mL distilled 1,4-dioxane. The reaction mixture was heated to reflux and stirred for 20 hours under air atmosphere. After most of the dioxane was removed under reduced pressure, the residue was added CH_3OH (20 mL $\times$ 3) to extract the products and to precipitate the catalyst, which was washed with 5 mL H_2O for three times, dried under reduced pressure, then used directly in the next run. The coupling product in the combined MeOH solution was obtained after purification by chromatography on a silica gel column.

(4) General procedure for the hydrogenations:

In a 50 mL glass-lined stainless steel reactor with a magnetic stirring bar was charged with 1 mmol substrates and 0.5 mol % **G₂DenP**-Pd and 10 mL $CHCl_3$. The autoclave was closed and was pressurized with H_2 (5 to 30 atm). The mixture was stirred under the H_2 pressure at 40 ~ 80 °C for several hours. After carefully venting hydrogen, most of the reaction solvent was removed under reduced pressure. The conversion of substrates and yield of products were determined by GC.

(5) Effect of base and solvent on the Suzuki coupling reactions:

Entry	Base	Solvent	Yield (%) ^a
1	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	EtOH/ H_2O (4/1)	73
2	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	Toluene	94
3	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	THF	91
4	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	DMF	92
5	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	Dioxane	97
6	$\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$	Dioxane/ H_2O (4/1)	97
7	NaOAc	Toluene	< 5
8	NaOAc	Tolunen/ H_2O (4/1)	45
9	K_2CO_3	Dioxane/ H_2O (4/1)	52
10	K_3PO_4 (anhydrous)	Dioxane	94
11	Et_3N	Dioxane	<10

^a Isolated yield.

3. ^1H NMR and ^{13}C NMR spectra data of the coupling products

Compound 1 : ^1H NMR (CDCl_3) δ 7.29-7.34 (m, 2H), 7.39-7.44 (m, 4H), 7.56-7.59 (m, 4H); ^{13}C NMR (CDCl_3) δ 127.22, 127.30, 128.80, 141.30.

Compound 2 : ^1H NMR (CDCl_3) δ 3.94 (s, 3H), 7.39-7.49 (m, 3H), 7.61-7.67 (m, 4H), 8.10 (d, J = 8.63 Hz, 2H); ^{13}C NMR (CDCl_3) δ 52.13, 127.06, 127.29, 128.15, 128.93, 130.11, 140.02, 145.65, 167.01.

Compound 3 : ^1H NMR (CDCl_3) δ 4.77 (s, 1H), 6.88-6.91 (m, 2H), 7.25-7.29 (m, 1H), 7.38-7.55 (m, 6H); ^{13}C NMR (CDCl_3) δ 155.65, 126.73, 128.41, 128.74, 134.10, 140.76, 155.03.

Compound 4 : ^1H NMR (CDCl_3) δ 2.64 (s, 3H), 7.42-7.50 (m, 3H), 7.62-7.70 (m, 4H), 8.04 (d, $J = 6.60$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 26.67, 127.24, 127.28, 128.24, 128.93, 128.97, 135.88, 139.89, 145.80, 197.76.

Compound 5 : ^1H NMR (CDCl_3) δ 3.88 (s, 3H), 7.31-7.47 (m, 4H), 7.56 (d, $J = 8.60$ Hz, 2H), 7.72 (d, $J = 7.75$ Hz, 1H), 7.97 (d, $J = 7.74$ Hz, 1H), 8.25 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 52.21, 127.18, 127.76, 128.29, 128.37, 128.88, 128.91, 130.71, 131.55, 140.13, 141.49, 167.08.

Compound 6 : ^1H NMR (CDCl_3) δ 7.34-7.41 (m, 3H), 7.55-7.58 (m, 2H), 7.66-7.68 (m, 2H), 7.87 (t, $J = 8.34$ Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (CDCl_3) δ 127.40, 127.71, 128.52, 129.06, 130.30, 135.21, 139.72, 147.18, 191.96.

Compound 7 : ^1H NMR (CDCl_3) δ 7.37-7.46 (m, 6H), 7.47-7.64 (m, 2H), 8.03 (d, $J = 7.74$ Hz, 1H), 9.98 (s, 1H); ^{13}C NMR (CDCl_3) δ 127.58, 127.79, 128.13, 128.45, 130.12, 130.79, 133.56, 133.75, 137.78, 145.98, 192.42.

Compound 8 : ^1H NMR (CDCl_3) δ 7.43-7.53 (m, 3H), 7.61-7.64 (m, 3H), 7.91 (d, $J = 7.74$ Hz, 1H), 8.19 (d, $J = 8.19$ Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (CDCl_3) δ 121.97, 122.04, 127.17, 128.55, 129.18, 129.72, 133.04, 138.69, 142.90, 148.76.

Compound 9 : ^1H NMR (CDCl_3) δ 7.29-7.32 (m, 2H), 7.39-7.45 (m, 5H), 7.59 (t, $J = 7.52$ Hz, 1H), 7.83 (d, $J = 7.92$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 124.09, 127.92, 128.21, 128.26, 128.72, 131.99, 132.32, 136.35, 137.43, 149.34.

Compound 10 : $^1\text{H NMR (CDCl}_3\text{)}$ δ 2.34 (s, 3H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.21-7.29 (m, 1H), 7.36 (t, $J = 6.24$ Hz, 2H), 7.42 (d, $J = 8.14$, 2H), 7.51-7.54 (m, 2H); $^{13}\text{C NMR (CDCl}_3\text{)}$ δ 21.06, 125.93, 125.95, 127.67, 128.44, 135.97, 137.31, 140.12.

Compound 11 : $^1\text{H NMR (CDCl}_3\text{)}$ δ 2.21 (s, 3H), 7.17-7.20 (m, 4H), 7.25-7.29 (m, 3H), 7.32-7.35 (m, 2H); $^{13}\text{C NMR (CDCl}_3\text{)}$ δ 20.47, 125.76, 126.76, 127.25, 128.07, 129.20, 129.80, 130.31, 135.36, 141.95, 141.98.

Compound 12 : $^1\text{H NMR (CDCl}_3\text{)}$ δ 2.33 (s, 3H), 3.86 (s, 3H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 8.1$ Hz, 2H), 7.57 (d, $J = 8.25$ Hz), 8.02 (d, $J = 8.25$ Hz, 2H). $^{13}\text{C NMR (CDCl}_3\text{)}$ δ 21.15, 52.07, 126.79, 127.11, 128.62, 129.65, 130.08, 137.11, 138.10, 145.58, 167.04.

Compound 13 : $^1\text{H NMR (CDCl}_3\text{)}$ δ 2.23 (s, 3H), 2.36 (s, 3H), 7.15-7.21 (m, 8H). $^{13}\text{C NMR (CDCl}_3\text{)}$ δ 20.55, 21.21, 125.79, 127.11, 128.82, 129.13, 129.90, 130.33, 135.44, 136.41, 139.11, 141.95.

Compound 14 : $^1\text{H NMR (CDCl}_3\text{)}$ δ 2.65 (s, 3H), 3.95 (s, 3H), 7.68-7.72 (m, 4H), 8.04-8.07 (m, 2H), 8.12-8.15 (m, 2H). $^{13}\text{C NMR (CDCl}_3\text{)}$ δ 26.68, 52.21, 127.23, 127.44, 128.98, 129.80, 130.23, 136.53, 144.21, 144.46, 166.75, 197.56.

Compound 15 : ^1H NMR (CDCl_3) δ 2.18 (s, 3H), 2.55 (s, 3H), 7.12-7.20 (m, 4H), 7.32-7.34 (m, 2H), 7.90-7.93 (m, 2H). ^{13}C NMR (CDCl_3) δ 19.34, 25.59, 124.91, 126.87, 127.18, 128.43, 128.46, 129.50, 134.11, 134.60, 139.73, 145.94, 196.74.

Compound 16 : ^1H NMR (CDCl_3) δ 3.86 (s, 3H), 7.03-7.09 (m, 2H), 7.46-7.53 (m, 4H), 7.99-8.03 (m, 2H). ^{13}C NMR (CDCl_3) δ 51.08, 114.68, 114.96, 125.83, 127.82, 127.93, 129.12, 135.05, 135.09, 143.52, 160.27, 163.56, 165.84.

Compound 17 : ^1H NMR (CDCl_3) δ 2.22 (s, 3H), 7.05 (t, J = 8.7 Hz, 3H), 7.17-7.26 (m, 6H). ^{13}C NMR (CDCl_3) 20.44, 114.84, 115.12, 125.86, 127.44, 129.83, 130.40, 130.68, 130.79, 135.41, 137.89, 137.94, 140.96, 160.34, 163.60.

Compound 18 : ^1H NMR (CDCl_3) δ 1.92 (s, 3H), 7.26-7.31 (m, 2H), 7.33-7.36 (m, 4H), 7.40-7.46 (m, 3H). ^{13}C NMR (CDCl_3) δ 30.43, 127.45, 127.89, 128.68, 128.87, 130.25, 130.70, 140.54, 140.76, 140.94, 204.83.

Compound 19 : ^1H NMR (CDCl_3) δ 7.21-7.25 (m, 1H), 7.41-7.50 (m, 3H), 7.73-7.76 (m, 2H), 7.98-8.01 (m, 2H), 8.69-8.70 (m, 1H). ^{13}C NMR (CDCl_3) δ 120.62, 122.12, 125.94, 126.77, 126.99, 136.83, 139.34, 149.63, 157.46.

Compound 20 : ^1H NMR (CDCl_3) δ 7.37-7.50 (m, 4H), 7.55-7.58 (m, 2H), 7.85-7.87 (m, 1H), 8.59 (d, J = 1.8Hz, 1H), 8.86 (d, J = 1.8Hz, 1H). ^{13}C NMR (CDCl_3) δ 123.61, 127.17, 128.15, 129.11, 134.47, 136.71, 137.78, 148.22, 148.35.

Compound 21 : ^1H NMR (CDCl_3) δ 7.43-7.51 (m, 5H), 7.62-7.65 (m, 2H), 8.65-8.67 (m, 2H). ^{13}C NMR (CDCl_3) δ 121.64, 126.99, 129.06, 129.12, 138.17, 148.36, 150.26.

Compound 22 : ^1H NMR (CDCl_3) δ 7.39-7.42 (m, 2H), 7.46-7.51 (m, 2H), 7.70-7.73 (m, 2H), 7.96-7.99 (m, 2H), 8.16-8.20 (m, 2H), 8.90-8.92 (m, 1H). ^{13}C NMR (CDCl_3) δ 121.47, 125.47, 127.46, 127.77, 128.47, 128.98, 129.23, 129.90, 136.25, 139.32, 140.29, 147.67, 150.34.

4. Spectra (^1H , ^{13}C , ^{31}P NMR) of ligand G_3DenP

^1H NMR of G_3DenP :

¹³C NMR of G₃DenP:

DDM

WL-61-63-P

10.318

Chemical structure of a dendritic molecule, likely a dendritic polymer or dendritic ligand. The structure features a central benzene ring substituted with a CH_2PPh_2 group and four CH_2O groups. Each CH_2O group is part of a chain that branches out into three phenyl rings at the periphery, creating a total of 12 terminal phenyl groups.

Current Data Parameters
NAME hou-31p
EXPNO 77
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050205
Time 14.56
INSTRUM AV400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 66227.211 Hz
FIDRES 1.038013 Hz
AQ 0.4817386 sec
RG 1024
DW 7.350 usec
DE 6.00 usec
TE 298.3 K
D1 1.00002000 sec
d11 0.03000200 sec
DELTA 0.89999998 sec
dCREST 0.00000000 sec
dCMIX 0.01500000 sec

***** CHANNEL f1 *****
NUC1 31P
P1 8.30 usec
PL1 -6.00 dB
SFO1 161.9771319 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 15.00 dB
PL13 17.00 dB
SFO2 400.1316025 MHz

F2 - Processing parameters
SI 32768
SF 161.9755292 MHz
MCW EM
SGB 0
LB 5.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 7.00 cm
F1F 200.000 GPP
F1 32299.11 Hz
F2D -100.600 ppm
F2 -16197.55 Hz
dHMC 13.63636 ppm/c
dCM 2008.75732 Hz/c

DDM

150

100

50

0

-50

5. Spectra (^{31}P NMR) of **G₃DenP-Pd** particles and **G₃DenP-Pd(0)** complex

^{31}P NMR of **G₃DenP-Pd(0)** Complex

In-situ preparation from [**G₃DenP** + Pd(dba)₂ (2/1)]

6. Spectra (^1H , ^{13}C NMR) of coupling products :

Compound 1 :

Compound 2 :

Compound 3 :

Compound 4 :

Compound 5 :

Compound 6 :

Compound 7 :

Compound 8 :

Compound 9 :

Compound 10 :

Compound 11 :

Compound 12 :

Compound 13 :

Compound 14 :

Compound 15 :

Compound 16 :

Compound 17 :

Compound 18 :

Compound 19 :

Compound 20 :

Compound 21 :

Compound 22 :