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Novel 3D Coordination Palladium–Network Complex: A Recyclable Catalyst for Suzuki–Miyaura Reaction†

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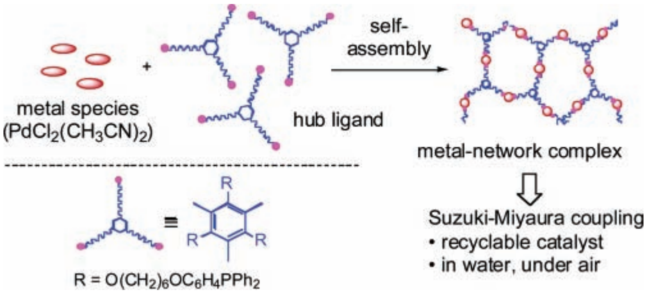
ABSTRACT



A novel solid-phase 3D metal–organic coordination network catalyst was prepared via self-assembly from $PdCl_2(CH_3CN)_2$ and a trisphosphine hub with three flexible alkyl-chain linkers. This insoluble network complex efficiently catalyzed the Suzuki–Miyaura reaction under atmospheric conditions in water. This catalyst was reused without loss of catalytic activity.

The development of metal−organic 3D coordination network complexes is an important topic for supramolecular chemistry. Their use in storage, channels, and catalysts already has attracted much attention.[1] However, the construction of recyclable catalytic systems using insoluble metal−organic 3D coordination network complexes has yet to be addressed.[2] Although complexes with a rigid linkage between metals and nonflexible organic ligands have been applied to heterogeneous catalysis and have been acknowledged as pioneering work in this field,[3] we believe that the development of novel 3D network catalyst systems with high activity and reusability still remains a major challenge. Having previously developed metal-cross-linked polymeric complexes via self-assembly of metal species with non-cross-linked polymer ligands (Scheme 1, top) that catalyze various organic transformations with high activity and reusability under heterogeneous conditions,[4] we then envisioned a self-assembling strategy for the preparation of metal-cross-linked polymeric complexes that could be applied to the construction of novel 3D coordination metal−network complexes

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† Y.M.A.Y. sincerely dedicates this manuscript to Prof. K. C. Nicolaou on the occasion of his 60th birthday.

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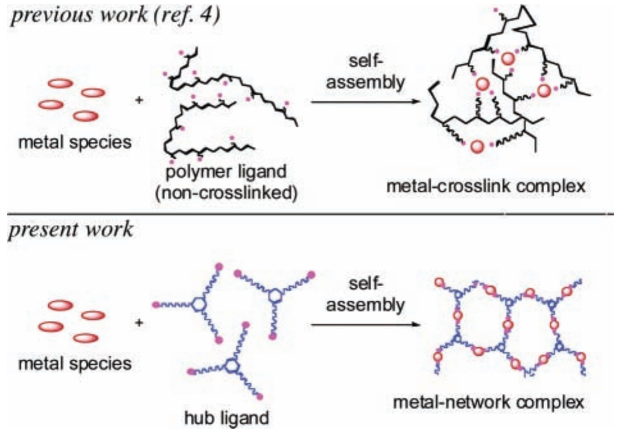
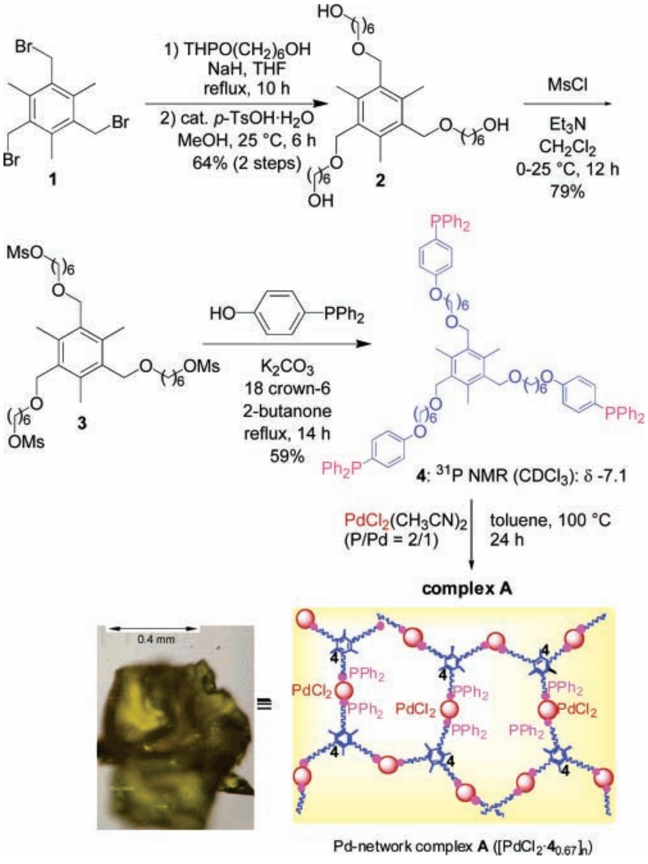
Scheme 1



using a metal species and a multicoordinating ligand monomer as the connecter and the hub of the molecular network, respectively. With catalytic utility in mind, we designed a metal−network complex of a C_3-trisphosphine with flexible alkyl-chain tethers and a palladium species through Pd−P coordination (Schemes 1 (bottom) and 2), where a palladium species serves as a connecter of the C_3-trisphosphine hub and as a catalytically active center.[5] Although this type of flexible alkyl-chain tether has not been used for the preparation of insoluble 3D metal−network complexes, hydrophobic alkyl-chain tethers would be critical in forming a pliable network to capture organic substrates efficiently in the matrix of a 3D palladium complex promoting a given catalytic reaction. In this communication, we would like to present the successful preparation of a 3D coordination metal−network complex of palladium, which showed high catalytic activity and recyclability in the Suzuki−Miyaura reaction in water under heterogeneous conditions.[4d,g,6,7] In the catalytic system, both the reaction and the workup were carried out only with water in the absence of organic solvents.

Scheme 2



A novel 3D palladium−network complex **A** was obtained by self-assembly of the $PdCl_2$ and C_3-trisphosphine **4**, which was prepared from the commercially available 2,4,6-tris(bromomethyl)mesitylene (**1**) in four steps (Scheme 2). Thus, etherification of the tribromide **1** with $THPO(CH_2)_6OH$, a component of the alkyl-chain tether, followed by removal of the tetrahydropyranyl groups gave the triol **2**. After mesylation of the triol **2**, the triarylphosphine groups were introduced by etherification of the resulting trimesylate **3** with 4-(diphenylphosphino)phenol to give the C_3-triphosphine **4** in 30% overall yield (four steps from **1**). A 3D coordination palladium−network complex was prepared by mixing $PdCl_2(CH_3CN)_2$ and 0.67 mol equiv of **4** (2 mol equiv of phosphine) in toluene at 100 °C for 24 h, during which complex **A** formed as a yellow gel from the reaction mixture. Complex **A** is insoluble in dichloromethane, chloroform, toluene, methanol, and water. To elucidate the structure of

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(4) For a review, see: (a) Yamada, Y. M. A. *Chem. Pharm. Bull*. **2005**, *53*, 723. For recent examples, see: (b) Yamada, Y. M. A.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Org. Lett.* **2001**, *3*, 1837. (c) Yamada, Y. M. A.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2002**, *43*, 3431. (d) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Org. Lett.* **2002**, *4*, 3371. (e) Yamada, Y. M. A.; Tabata, H.; Takahashi, H.; Ikegami, S. *Synlett* **2002**, 2031. (f) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2003**, *44*, 2379. (g) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *J. Org. Chem.* **2003**, *68*, 7733. (h) Yamada, Y. M. A.; Tabata, H.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2004**, *60*, 4087. (i) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2004**, *60*, 4097. (j) Hamamoto, H.; Suzuki, Y.; Yamada, Y. M. A.; Tabata, H.; Takahashi, H.; Ikegami, S. *Angew. Chem., Int. Ed*. **2005**, *44*, 4536. (k) Yamada, Y. M. A.; Uozumi, Y. *Org. Lett.* **2006**, *8*, 1375.

(5) Cage-structured platinum complexes with trisphosphines have been reported. (a) Lindner, E.; Hermann, C.; Baum, G.; Fenske, D. *Eur. J. Org. Chem*. **1999**, 679. (b) Lindner, E.; Khanfar, M.; Steimann, M. *Eur. J. Org. Chem*. **2001**, 2411.

(6) We have already reported PS−PEG resin-supported Pd catalysts for the Suzuki−Miyaura reaction in water; see: (a) Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem*. **1999**, *64*, 3384. (b) Uozumi, Y.; Nakai, Y. *Org. Lett*. **2002**, *4*, 2997. (c) Uozumi, Y.; Kikuchi, M. *Synlett* **2005**, 1775.

(7) For reviews, see: (a) Uozumi, Y. *Top. Curr. Chem.* **2004**, *242*, 77. (b) Frenzel, T.; Solodenko, W.; Kirschning, A. In *Polymeric Materials in Organic Synthesis and Catalysis*; Buchmeiser, M. R., Ed.; Wiley-VCH: Weinheim, 2003; p 201. (c) Leadbeater, N. E. *Chem. Commun.* **2005**, 2881. (d) Bai, L.; Wang, J.-X. *Curr. Org. Chem.* **2005**, *9*, 535. (e) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed*. **2005**, *44*, 4442 and references therein. For selected recent examples, see: (f) Thiot, C.; Schmutz, M.; Wagner, A.; Mioskowski, C. *Angew. Chem., Int. Ed*. **2006**, *45*, 2868. (g) Nishio, R.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2005**, *7*, 4831. (h) Solodenko, W.; Schön, U.; Messinger, J.; Glinschert, A.; Kirschning, A. *Synlett* **2004**, 1699. (i) Baleizão, C.; Corma, A.; García, H.; Leyva, A. *J. Org. Chem.* **2004**, *69*, 439. (j) Tzchucke, C. C.; Bannwarth, W. *Helv. Chim. Acta* **2004**, *87*, 2882. (k) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc*. **2002**, *124*, 11572. (l) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc*. **2002**, *124*, 7642. (m) Gordon, R. S.; Holmes, A. B. *Chem. Commun*. **2002**, 640.

complex **A**, several micro- and spectroscopic measurements were carried out. The morphology of **A** was evaluated by optical- and scanning electron-microscopic (SEM) observations, which confirmed **A** to be blocklike and 50−500 μm wide (Figure 1A). An energy dispersive spectrum (EDS) collected in the SEM exhibited the presence of Pd, Cl, and P in the complex (Figure 1C). In the gel-phase $^{31}P\{^{1}H\}$ MAS NMR study of complex **A**, the narrow singlet at δ −7.1 ppm observed for the starting triphosphine **4** disappeared and was replaced by a new resonance at δ +20 ppm (Figure 1B). The remarkable low-field shift demonstrates that the triarylphosphino unit of **4** coordinates to the palladium forming a $PdCl_2(PAr_3)_2$ complex (connecter−hub complex) in the gel matrix.

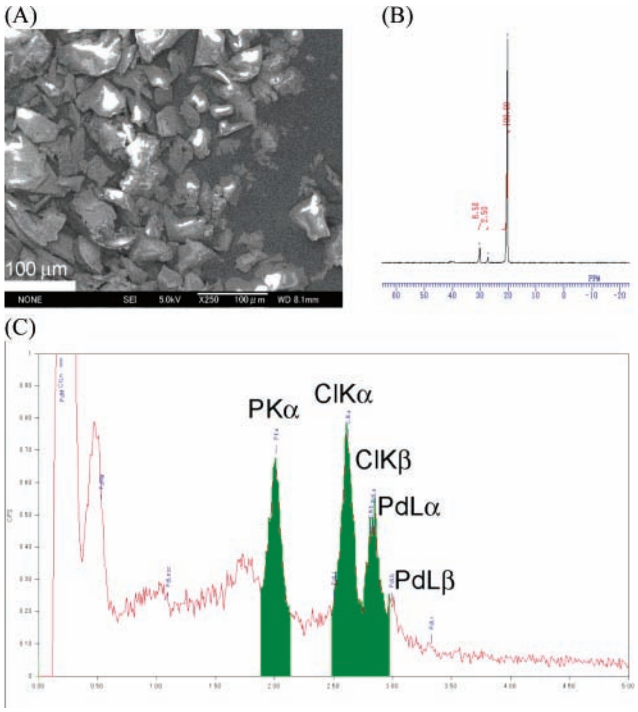
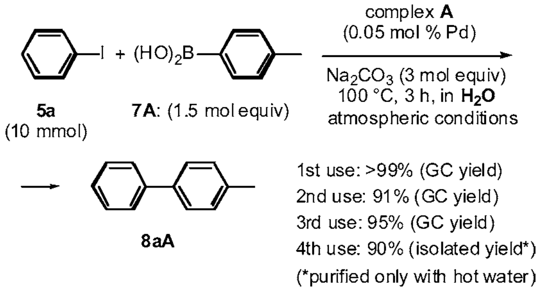


Figure 1. Microscopic and spectroscopic data of complex **A**. (A) SEM image; (B) $^{31}P\{^{1}H\}$ NMR spectrum; (C) EDS spectrum.

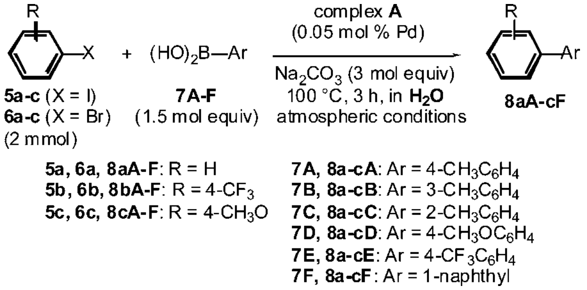
To explore the catalytic potential of the palladium−network complex **A**, we elected to study the Suzuki−Miyaura reaction, the palladium-catalyzed cross-coupling of aryl halides with arylboronic acids, which is recognized as one of the most powerful carbon−carbon bond-forming reactions.[8] We were pleased to find that the network complex catalyzed the coupling reaction under atmospheric conditions in water without organic solvents to achieve a high level of chemical greenness. The reaction of iodobenzene (**5a**) with *p*-tolylboronic acid (**7A**) (1.5 mol equiv) took place smoothly with 0.05 mol % of Pd of complex **A** in an aqueous solution of Na_2CO_3 (3 mol equiv) at 100 °C for 3 h under atmospheric conditions to give the 4-methyl biphenyl (**8aA**) in quantitative yield. After the first reaction, the recovered catalyst was successively subjected to a second, third, and fourth series of the reaction under similar conditions to afford 91%, 95%, and 90% yield of **8aA**, respectively. In the fourth run, the product was isolated using hot water without use of organic solvents.[4g,9] Thus, after completion of the reaction, the reaction mixture was filtered with boiling water to recover the insoluble complex **A**. The aqueous filtrate was cooled to 25 °C to give **8aA** as colorless crystals (Scheme 3).

Scheme 3



With a practical and green catalytic protocol for the Suzuki−Miyaura reaction in hand, we next examined the coupling of a variety of aryl halides and arylboronic acids in water (Scheme 4 and Table 1). Twenty-seven combinations of six varieties of aromatic halides and six varieties of arylboronic acids were subjected to the coupling in aqueous Na_2CO_3 at 100 °C for 3 h using 0.05 mol % of palladium of complex **A**. Electron-deficient as well as electron-rich aryl halides readily coupled with arylboron reagents bearing *para*-, *meta*-, and *ortho*-EWG and EDG substituents to give the corresponding biaryls in 80 → 99% yields.

Scheme 4



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(9) After completion of the reaction, the reaction mixture (100 °C) was filtered through a glass filter at 100 °C, and the collected polymeric catalyst was rinsed with hot water. The filtrate was cooled to 25 °C to precipitate colorless crystals of **8aA** at the top of the water phase. They were collected by filtration, washed with water, and dried in vacuo.

(10) These products were isolated via chromatographic purification of the samples that were used for GC analysis.

Table 1. Suzuki–Miyaura Reaction of Aryl Halides with Arylboronic Acids Catalyzed by Complex **A** in Water[a]

entry	**5** or **6**	**7**	**8**	yield (%)[b]	entry	**5** or **6**	**7**	**8**	yield (%)[b]
1	**5a**	**7A**	**8aA**	>99	15	**5c**	**7D**	**8cD**	92
2	**5a**	**7B**	**8aB**	91	16	**5c**	**7E**	**8cE**	85
3	**5a**	**7C**	**8aC**	99[c]	17	**5c**	**7F**	**8cF**	98[c]
4	**5a**	**7D**	**8aD**	99[c]	18	**6a**	**7A**	**8aA**	80
5	**5a**	**7E**	**8aE**	91	19	**6a**	**7B**	**8aB**	92
6	**5a**	**7F**	**8aF**	92	20	**6a**	**7C**	**8aC**	98
7	**5b**	**7A**	**8bA**	94	21	**6a**	**7D**	**8aD**	92
8	**5b**	**7B**	**8bB**	99[c]	22	**6b**	**7A**	**8bA**	85
9	**5b**	**7C**	**8bC**	95	23	**6b**	**7B**	**8bB**	94
10	**5b**	**7D**	**8bD**	96[c]	24	**6b**	**7C**	**8bC**	96
11	**5b**	**7E**	**8bE**	>99	25	**6b**	**7D**	**8bD**	83
12	**5b**	**7F**	**8cF**	91	26	**6b**	**7E**	**8bE**	99
13	**5c**	**7B**	**8cB**	82	27	**6c**	**7C**	**8cC**	84
14	**5c**	**7C**	**8cC**	91					

[a] All the reactions were carried out in the presence of 0.05 mol % of palladium of the catalyst and Na_2CO_3 (3 mol equiv) in water (1 mmol of **5**/2 mL of H_2O) at 100 °C for 3 h under atmospheric conditions. **5** or **6**/**7** = 1.0/1.5. [b] GC yield, unless otherwise noted. [c] Isolated yield.[10]

In conclusion, a novel 3D coordination metal–network complex **A** of the $PdCl_2$ connector with a C_3-trisphosphine hub ligand was developed as an aqua-catalytic insoluble composite. The Suzuki–Miyaura reaction of a variety of aryl halides with arylboronic acids took place with the insoluble network complex **A** to afford the desired products in high yields. The catalyst **A** promoted the reaction under atmospheric conditions in water with recyclability. Applications of the metal–network complexation with other metal species for various catalytic reaction systems are currently under study in our labs.

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Supporting Information Available: Experimental procedures and characterization data, including ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and GC-MS spectra of ligand **4**, complex **A**, and the Suzuki–Miyaura coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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