Published in final edited form as:

ACS Macro Lett. 2013 January 15; 2(1): 10–13. doi:10.1021/mz300479b.

***t*-Bu₃P-Coordinated 2-Phenylaniline-Based Palladacycle Complex as a Precatalyst for the Suzuki Cross-coupling Polymerization of Aryl Dibromides with Aryldiboronic Acids**

Hong-Hai Zhang, Chun-Hui Xing, Georges Bouobda Tsemo, and Qiao-Sheng Hu*

Department of Chemistry, College of Staten Island and the Graduate Center of the City University of New York, Staten Island, New York 10314

Abstract

t-Bu₃P-Coordinated 2-phenylaniline-based palladacycle complex, [2'-(amino-*k*M)[1,1'-biphenyl]-2-yl-*k*C]chloro(tri-*t*-butylphosphine)palladium, as a general, highly efficient precatalyst for the Suzuki cross-coupling polymerization of aryl dibromides with aryldiboronic acids is described. Such *t*-Bu₃P-coordinated 2-aminobiphenyl-based palladacycle complex-catalyzed Suzuki cross-coupling polymerization afforded polymers within an hour, with the yields and the molecular weights comparable to or higher than that of polymers obtained by using other palladium catalysts with much longer polymerization time. Our study provided a highly efficient catalyst system for the Suzuki cross-coupling polymerization of aryl dihalides with aryldiboronic acids. Our study also paved the road for us to investigate other monodentate ligand-coordinated palladacycle complexes including *N*-heterocyclic carbene-coordinated ones for cross-coupling polymerizations.

Keywords

Suzuki Cross-Coupling; Polymerization; Palladium(0); Aryldibromides; Aryldiboronic acids

The Pd(0)-catalyzed Suzuki cross-coupling polymerization (SCCP) of aryl dihalides with aryldiboronic acids/acid esters has become arguably the most powerful method for the synthesis of an array of poly(arylene)s,^{1,2} which are useful materials with applications in fields ranging from semiconductors, sensors to optoelectronics. Despite the widespread applications, reported SCCPs often suffered from shortcomings including lengthy reaction time, typically 24 hours or longer even under refluxing conditions, low polymerization yields and difficulty to achieve high molecular weight (degree of polymerization).³ Scrutiny of reported SCCPs suggested that these shortcomings can mainly be attributed to the direct Pd catalyst adoption approach: the palladium catalysts employed for the SCCPs were commonly adopted directly from the Suzuki cross-coupling reactions of aryl halides and arylboronic acids. Unlike the standard Suzuki cross-coupling reactions, in which only one catalytic cycle is involved for the product formation, multiple consecutive catalytic cycles are involved for the product formation in the SCCPs. Such a Pd catalyst adoption approach amplifies problems that may not be pronounced for standard Suzuki cross-coupling reactions, e. g., low catalytic activities of the catalysts, the decomposition of the catalysts, etc., causing the aforementioned shortcomings for the SCCPs. Development of palladium

*Corresponding Author: Qiaosheng.hu@csi.cuny.edu.

Supporting Information. General procedures and product characterization of Pd(0)-catalyzed cross-coupling polymerization of aryl dibromides and aryldiboronic acids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

catalysts that can attenuate the problems caused by the multiple consecutive catalytic cycle nature of polymerization is expected to overcome shortcomings associated with reported palladium catalysts for the SCCP and could thus be valuable for the field of conjugated polymer synthesis.

We speculated that the problems caused by the direct Pd catalyst adoption approach might in large part be due to the relatively low catalytic activity of reported Pd catalysts, which rendered the oxidative addition step in reported SCCPs likely the rate-determining step. The slow oxidative addition would allow the Pd(0) catalyst to decompose and the amplification of such a catalyst decomposition would cause aforementioned shortcomings for reported SCCPs. We thus reasoned that Pd(0) catalysts with high oxidative addition rates, *e. g.*, 12-electron LPd(0) species with bulky, electron-rich monodentate ligands such as *t*-Bu₃P,^{4,5} could alter the rate-determining step from the oxidative addition step to the transmetalation step. Such a switch could minimize the catalyst decomposition and might address the problems caused by the multiple consecutive catalytic cycle nature of polymerization. Thus, 12-electron LPd(0) species with bulky, electron-rich monodentate ligands such as *t*-Bu₃P could be efficient catalysts for the Suzuki cross-coupling polymerizations. Based on the consideration that the generation of 12-electron LPd(0) species should not involve the participation of AA or BB monomers, which could alter the ratio and the nature of the monomers, and recent elegant reports on generating Pd(0) species from palladacycle complexes and bases,^{6,7} we envisioned that monodentate ligand-coordinated palladacycle complexes **1** could be suitable precatalysts to generate the desired 12-electron LPd(0) catalysts for the SCCP (Scheme 1). In this communication, we report our preliminary results on establishing *t*-Bu₃P-coordinated 2-phenylaniline-based palladacycle complex **1a**, as well as three other monophosphine-coordinated palladacycles **1b–d**^{7–9} (Chart 1), as a general, highly efficient precatalyst for the fast Suzuki cross-coupling polymerization.

t-Bu₃P-coordinated 2-phenylaniline-based palladacycle complex **1a** was prepared from 2-phenylaniline in 58% yield by a one-pot, two-step sequence (Scheme 2), similar to the reported synthesis of **1b** and **1d**.^{7–9} **1a** is air/moisture-stable. **1c** was prepared in a similar way with a moderate yield from Cy₃P.⁹

Based on the consideration that the transmetalation step could likely be the rate-determining step with 12-electron (*t*-Bu₃P)Pd(0) species as the catalysts and could be influenced by a base,¹ our study began with the examination of different bases for the polymerization of dibromide **2a** and diboronic acid **3a**. The polymerizations were performed in THF at 60 °C for one hour. We found with **1a** as the precatalyst, among the bases examined (entries 1–5), K₂CO₃, K₃PO₄ and K₂HPO₄ were found to be good bases (Table 1, entries 1, 4, 5), with K₃PO₄ being the best one (Table 1, entry 4). Further examination revealed the use of 4 equivalents of K₃PO₄ generated the polymer with the highest molecular weight (Table 1, entries 4, 6–8). Palladium catalysts derived from Pd₂(dba)₃/*t*-Bu₃P (0.5:1), Pd₂(dba)₃/*t*-Bu₃P (0.5:2),¹⁰ Pd(*t*-Bu₃P)₂,¹¹ PhPd(*t*-Bu₃P)Br¹² and [*t*-Bu₃PPdBr]₂¹³ were also employed for the polymerization under the same reaction condition. These Pd catalysts exhibited much lower catalytic efficiency than palladacycle complex **1a**, as evidenced by the much lower molecular weights of the products (*M_n* = 2 300 – 3 900) (Table 1, entries 9–13). For comparison purpose, other monophosphine-coordinated 2-aminobiphenyl-based palladacycle complexes **1b**,⁸ **1c**⁹ and **1d**,^{7b} Pd(PPh₃)₄, Pd(OAc)₂/XPhos (1:2), Pd₂(dba)₃/XPhos (0.5:2), Pd(OAc)₂/XPhos (1:1), Pd₂(dba)₃/XPhos (0.5:1), Pd(OAc)₂/*o*-Tol₃P (1:1) and Pd(OAc)₂/*o*-Tol₃P (1:2)^{3d} complexes were also employed for the polymerization under the same reaction condition. We found that while these Pd catalysts exhibited much lower catalytic efficiency than **1a**, as evidenced by the much lower molecular weights of the products (*M_n* = 1 900 – 8 900) (Table 1, entries 14–23), palladacycle complexes **1b** and **1d** were again observed to exhibit higher catalytic efficiency over conventional Pd catalysts

Pd(PPh₃)₄, Pd(OAc)₂/XPhos, Pd₂(dba)₃/XPhos and Pd(OAc)₂/*o*-Tol₃P (1:2) (Table 1, entry 14 vs. 15; entry 17 vs. 18–21). These results demonstrated *t*-Bu₃P-coordinated 2-aminobiphenyl-based palladacycle complex **1a** was a highly efficient precatalyst for the SCCPs.

With *t*-Bu₃P-coordinated 2-aminobiphenyl-based palladacycle complex **1a** as the precatalyst, the Suzuki cross-coupling polymerization of a number of aryl dibromides with aryldiboronic acids were examined and our results are listed in Table 2. As shown in Table 2, **1a**-catalyzed Suzuki cross-coupling polymerization afforded polymers in high yields within an hour, with the molecular weights of the polymers in the range that would require the polymerization time of 24 hours or longer for polymerization processes catalyzed by other Pd catalysts (Table 2, entries 1–10). For direct comparison purpose, the Suzuki cross-coupling polymerization of (3,5-dibromophenyl)ferrocenylmethanol (**2f**) with 2,5-dihexoxy-1,4-phenyldiboronic acid (**3a**) and 2,7-dibromo-9,9-dioctylfluorene (**2e**) with 9,9-dihexyl-2,7-fluorenyldiboronic acid (**3b**) were also examined. We found that **1a**-catalyzed polymerization of **2f** with **3a** afforded a polymer with a molecular weight of $M_n = 8\ 200$ (GPC value, polystyrene standards) (Table 2, entry 9), whereas Pd(PPh₃)₄-catalyzed polymerization of **2f** with **3a** generated a polymer with a molecular weight of $M_n = 2\ 800$ under the condition of refluxing 24 hours in THF-H₂O.^{3f} **1a**-Catalyzed polymerization of **2e** with **3b** produced the polymer with a molecular weight of $M_n = 82\ 900$ (Table 2, entry 10), which was comparable to the molecular weights obtained by using other palladium catalysts with much longer polymerization time (50 °C, 3 days or 90 °C, 24 hours).^{14,15} These results further confirmed **1a** was a highly efficient precatalyst for the SCCP. In addition, polymers with higher molecular weights could be readily obtained by simply lengthening the reaction time (Table 2, entries 7 vs. 11, 8 vs. 12), demonstrating the stability of **1a** under the Suzuki cross-coupling polymerization and its ability to catalyze the Suzuki cross-coupling polymerization with high degree of polymerization.

In summary, based on the hypothesis that the use of 12-electron LPd(0) species as catalysts for the SCCP could alter the rate-determining step from the oxidative addition step to the transmetalation step and could overcome the problems associated with reported Pd catalysts for SCCP, we demonstrated that readily available, air/moisture-stable *t*-Bu₃P-coordinated 2-aminobiphenyl-based palladacycle complex, [2'-(amino-kN)[1,1'-biphenyl]-2-yl-kC]chloro(tri-*t*-butylphosphine)palladium, was a general, highly efficient precatalyst for the Suzuki cross-coupling polymerization of aryl dibromides with aryldiboronic acids. Such *t*-Bu₃P-coordinated 2-phenylaniline-based palladacycle complex-catalyzed Suzuki cross-coupling polymerization afforded polymers within an hour, with the yields and molecular weights comparable to or higher than that of polymers obtained by using other palladium catalysts with much longer polymerization time (24 hours or longer under refluxing conditions). Our study provided a highly efficient precatalyst for the Suzuki cross-coupling polymerization of aryl dihalides with aryldiboronic acids. This *t*-Bu₃P-coordinated 2-aminobiphenyl-based palladacycle complex might also be useful for other cross-coupling reactions including polymerizations. In addition, our study paved the road for us to investigate other monodentate ligand-coordinated palladacycle complexes including *N*-heterocyclic carbene-coordinated ones⁵ for cross-coupling polymerizations. Work towards these directions is currently underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We gratefully thank the NSF (CHE0911533) and NIH (1R15 GM094709) for funding. Partial support from PSC-CUNY Research Award Programs is also acknowledged.

ABBREVIATIONS

SCCP Suzuki cross-coupling polymerization

References

1. For recent reviews on Suzuki cross-coupling reactions: Miyaura N. *Topics in Current Chem.* 2002; 219:11–59. Suzuki A. *J Organomet Chem.* 1999; 576:147–168. Littke AF, Fu GC. *Angew Chem Int Ed.* 2002; 41:4176–4211. Díez-González S, Marion N, Nolan SP. *Chem Rev.* 2009; 109:3612–3676. [PubMed: 19588961] Darses S, Genet J-P. *Chem Rev.* 2008; 108:288–325. [PubMed: 18095714] Yin L, Liebscher J. *Chem Rev.* 2007; 107:133–173. [PubMed: 17212474]
2. For recent reviews on Suzuki cross-coupling polymerizations: Hu QS, Pu L, Itsuno S. *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis.* Wiley Hoboken 2011:323–364. Sakamoto J, Rehahn M, Wegner G, Schlueter AD. *Macromol Rap Commun.* 2009; 30:653–687. Hu QS, Rogers M, Long T. *Synthetic Methods for Step-Growth Polymers.* Wiley Hoboken 2003:467–526. Schluter AD. *J Polym Sci, Polym Chem Ed.* 2001; 39:1533–1556.
3. For recent examples: Goodson FE, Wallow TI, Novak BM. *Macromolecules.* 1998; 31:2047–2056. Hargadon MT, Davey EA, McIntyre TB, Gnanamgari D, Wynne CM, Swift RC, Zimbalist JR, Fredericks BL, Nicastro AJ, Goodson FE. *Macromolecules.* 2008; 41:741–750. Park MJ, Lee J, Park JH, Lee SK, Lee JI, Chu HY, Hwang DH, Shim HK. *Macromolecules.* 2008; 41:3063–3070. Murage J, Eddy JW, Zimbalist JR, McIntyre TB, Wagner ZR, Goodson FE. *Macromolecules.* 2008; 41:7330–7338. Kappaun S, Zelzer M, Bartl K, Saf R, Stelzer F, Slugovc C. *J Polym Science Part A: Polymer Chem.* 2006; 44:2130–2138. Hu QS, Tang ZY, Lu Y, Yu HB. *J Am Chem Soc.* 2003; 125:2856–2857. [PubMed: 12617635]
4. For recent reviews on LPd(0) complexes with t-Bu₃P as ligand for cross-coupling reactions: Fu GC. *Acc Chem Res.* 2008; 41:1555–1564. [PubMed: 18947239] Christmann U, Vilar R. *Angew Chem, Int Ed.* 2005; 44:366–374. Littke AF, Fu GC. *Angew Chem, Int Ed.* 2002; 41:4176–4211.
5. For recent reviews on LPd(0) complexes with N-heterocyclic carbenes as ligands for cross-coupling reactions: Marion N, Nolan SP. *Acc Chem Res.* 2008; 41:1440–1449. [PubMed: 18774825] Würtz S, Glorius F. *Acc Chem Res.* 2008; 41:1523–1533. [PubMed: 18720995] Kantchev EAB, O'Brien CJ, Organ MG. *Angew Chem, Int Ed.* 2007; 46:2768–2813. Díez-González S, Nolan SP. *Top Organomet Chem.* 2007; 21:47–82.
6. For recent reviews of palladacycles for cross-coupling reactions: Dupont J, Consorti CS, Spencer J. *Chem Rev.* 2005; 105:2527–2572. [PubMed: 15941221] Beletskaya IP, Cheprakov AV. *J Organomet Chem.* 2004; 689:4055–4082. Bedford RB. *Chem Commun.* 2003:1787–1796.
7. Biscoe MR, Fors B, Buchwald SL. *J Am Chem Soc.* 2008; 130:6686–6687. [PubMed: 18447360] Kinzel T, Zhang Y, Buchwald SL. *J Am Chem Soc.* 2010; 132:14073–14075. [PubMed: 20858009] Also see: Li PF, Buchwald SL. *Angew Chem, Int Ed.* 2011; 50:6396–6400. Shu W, Pellegatti L, Oberli MA, Buchwald SL. *Angew Chem, Int Ed.* 2011; 50:10665–10669. Noel T, Musacchio AJ. *Org Lett.* 2011; 13:5180–5183. [PubMed: 21899298] Kim J, Movassaghi M. *J Am Chem Soc.* 2011; 133:14940–14943. [PubMed: 21875056] Koenig M, Reith LM, Monkowius U, Knoer G, Bretterbauer K, Schoefberger W. *Tetrahedron.* 2011; 67:4243–4252. [PubMed: 21760646] Schmink JR, Krska SW. *J Am Chem Soc.* 2011; 133:19574–19577. [PubMed: 22070616] Molander GA, Trice SLJ, Kennedy SM, Dreher SD, Tudge MT. *J Am Chem Soc.* 2012; 134:11667–11673. [PubMed: 22769742] VanVeller B, Schipper DJ, Swager TM. *J Am Chem Soc.* 2012; 134:7282–7285. [PubMed: 22510100]
8. Albert J, Granell J, Zafrilla J, Font-Bardia M, Solans X. *J Organometallic Chem.* 2005; 690:422–429.
9. Gorelsky SI, Lapointe D, Fagnou K. *J Org Chem.* 2012; 77:658–668. [PubMed: 22148641]
10. Littke AF, Dai C, Fu GC. *J Am Chem Soc.* 2000; 122:4020–4028.

11. Yoshida T, Otsuka S. *J Am Chem Soc.* 1977; 99:2134–2140. Also see Paul F, Patt J, Hartwig JF. *Organometallics.* 1995; 14:3030–3039.
12. Huang W, Su L, Bo Z. *J Am Chem Soc.* 2009; 131:10348–10349. [PubMed: 19586020]
13. Stambuli JP, Kuwano R, Hartwig JF. *Angew Chem, Int Ed.* 2002; 41:4746–4748. Also see Proutiere F, Aufiero M, Schoenebeck F. *J Am Chem Soc.* 2012; 134:606–612. [PubMed: 22132686]
14. Eddy JW, Davey EA, Malsom RD, Ehle AR, Kassel S, Goodson FE. *Macromolecules.* 2009; 42:8611–8614.
15. Liu J, Shao S, Chen L, Xie Z, Cheng Y, Geng Y, Wang L, Jing X, Wang F. *Adv Mater.* 2007; 19:1859–1863.

Scheme 1.
 Monodentate Ligand-Coordinated 2-Phenylaniline-Based Palladacycle Complexes for Suzuki Cross-Coupling Polymerizations

Scheme 2. Preparation of $t\text{-Bu}_3\text{P}$ -Coordinated 2-Phenylaniline-Based Palladacycle Complex **1a**

1a: L = *t*-Bu₃P**1b:** L = PPh₃**1c:** L = PCy₃

Chart 1.
Monophosphine-Coordinated 2-Phenylaniline-Based Palladacycle Complexes

Table 1

Pd-Catalyzed Suzuki Cross-Coupling Polymerization^a

Entry	Catalyst	Base	Yield (%) ^b	M _n (PDI) ^c
1	1a	K ₂ CO ₃ (4 eq)	74	19 400 (2.33)
2	1a	Na ₂ CO ₃ (4 eq)	69	3 400 (1.47)
3	1a	KF (4 eq)	54	2 600 (1.28)
4	1a	K ₃ PO ₄ (4 eq)	85	20 100 (2.25)
5	1a	K ₂ HPO ₄ (4 eq)	75	19 000 (2.23)
6	1a	K ₃ PO ₄ (2 eq)	50	2 100 (1.28)
7	1a	K ₃ PO ₄ (3 eq)	50	2 000 (1.11)
8	1a	K ₃ PO ₄ (6 eq)	74	18 500 (2.37)
9	Pd ₂ (dba) ₃ + <i>t</i> -Bu ₃ P (0.5:2)	K ₃ PO ₄ (4 eq)	30	2 300 (1.05)
10	Pd ₂ (dba) ₃ + <i>t</i> -Bu ₃ P (0.5:1)	K ₃ PO ₄ (4 eq)	60	3 900 (1.48)
11	Pd(<i>t</i> -Bu ₃ P) ₂	K ₃ PO ₄ (4 eq)	51	2 600 (1.22)
12	PhPd(<i>t</i> -Bu ₃ P)Br	K ₃ PO ₄ (4 eq)	58	2 700 (1.27)
13	[<i>t</i> -Bu ₃ PPdBr] ₂	K ₃ PO ₄ (4 eq)	51	3 100 (1.35)
14	1b	K ₃ PO ₄ (4 eq)	41	2 600 (1.14)
15	Pd(PPh ₃) ₄	K ₃ PO ₄ (4 eq)	32	1 200 (1.13)
16	1c	K ₃ PO ₄ (4 eq)	33	2 500 (1.05)
17	1d	K ₃ PO ₄ (4 eq)	89	8 900 (2.42)
18	Pd ₂ (dba) ₃ + Xphos (0.5:2)	K ₃ PO ₄ (4 eq)	68	2 200 (1.46)
19	Pd(OAc) ₂ + Xphos (1:2)	K ₃ PO ₄ (4 eq)	64	2 600 (1.47)
20	Pd ₂ (dba) ₃ + Xphos (0.5:1)	K ₃ PO ₄ (4 eq)	55	2 900 (1.65)
21	Pd(OAc) ₂ + Xphos (1:1)	K ₃ PO ₄ (4 eq)	72	1 900 (1.27)
22	Pd(OAc) ₂ + <i>o</i> -Tol ₃ P (1:1)	K ₃ PO ₄ (4 eq)	64	2 900 (1.41)
23	Pd(OAc) ₂ + <i>o</i> -Tol ₃ P (1:2)	K ₃ PO ₄ (4 eq)	69	2 500 (1.29)

^aPolymerization condition: diboronic acid (1 equiv.), dibromide (1.02 equiv.), Pd catalyst (2 mol%), base (1 – 4 equiv.), THF, 60 °C, 1 h.^bIsolated yield.^cGPC analysis (polystyrene as standard, THF, 40 °C).

Table 2

Palladacycle Complex **1a**-Catalyzed Suzuki Cross-Coupling Polymerization of Aryl Dibromides with Aryldiboronic Acids^a

Entry	Br-Ar-Br	(HO) ₂ B-Ar'-B(OH) ₂	Yield ^b	M _n (PDI) ^c
1	(2a)	(3a)	85%	19 800 (2.30)
2	2a	(3b)	93%	11 200 (2.28)
3	(2b)	3b	99%	43 000 (2.54)
4	(2c)	3a	95%	8 800 (1.98)
5	(2d)	3a	87%	20 700 (2.39)
6	2d	3b	90%	19 100 (2.94)
7	(2e)	3a	97%	19 400 (2.39)
8	2e	3b	99%	43 000 (2.20) ^d

Entry	Br-Ar-Br	(HO) ₂ B-Ar'-B(OH) ₂	Yield ^b	M _n (PDI) ^c
9	(2f)	3a	94%	8 200 (1.70)
10	2e	(3c)	99%	82 900 (2.36)
11	2d	3b	99%	49 400 (3.81) ^e
12	2e	3b	99%	89 800 (2.44)

^a Polymerization condition: dibromide (1.02 equiv.), diboronic acid (1 equiv.), Pd catalyst (2 mol%), K₃PO₄ (4 equiv.), THF, 60 °C, 1 h.

^b Isolated yields.

^c GPC analysis (polystyrene as standard, THF, 40 °C) (average of two runs).

^d Reaction time: 20 minutes.

^e Reaction time: 2 h.