

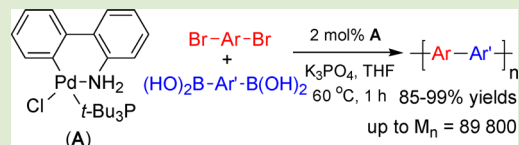
t-Bu₃P-Coordinated 2-Phenylaniline-Based Palladacycle Complex as a Precatalyst for the Suzuki Cross-Coupling Polymerization of Aryl Dibromides with Aryldiboronic Acids

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S Supporting Information

ABSTRACT: *t*-Bu₃P-coordinated 2-phenylaniline-based palladacycle complex, [2'-(amino-κN)[1,1'-biphenyl]-2-yl-κC]chloro(*tert*-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.



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 and sensors to optoelectronics. Despite the widespread applications, reported SCCPs often suffered from shortcomings including lengthy reaction time, typically 24 h or longer even under refluxing conditions, low polymerization yields, and difficulty achieving 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, for example, low catalytic activities of the catalysts, the decomposition of the catalysts, and so on, causing the aforementioned shortcomings for the SCCPs. Development of palladium 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, for example, 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.

Received: September 18, 2012

Accepted: December 11, 2012

Published: December 14, 2012

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

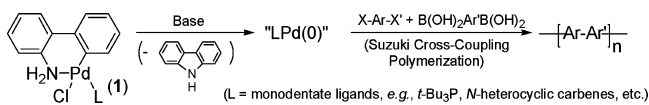
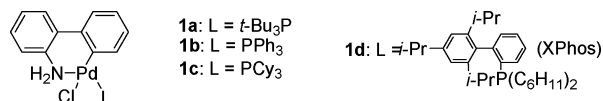
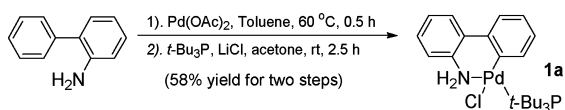


Chart 1. Monophosphine-Coordinated 2-Phenylaniline-Based Palladacycle Complexes



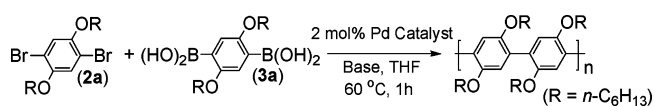
t-Bu₃P-coordinated 2-phenylaniline-based palladacycle complex **1a** was prepared from 2-phenylaniline in 58% yield by a one-pot, two-step sequence (Scheme 2), similar to the reported synthesis of **1b** and **1d**.^{7–9} Compound **1a** is air/moisture-stable, and **1c** was prepared in a similar way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

Scheme 2. Preparation of *t*-Bu₃P-Coordinated 2-Phenylaniline-Based Palladacycle Complex **1a**



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, our study began with the examination of different bases for the polymerization of dibromide **2a** and diboronate **3a**. The polymerizations were performed in THF at 60 °C for 1 h. 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 equiv 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)Br,¹² 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 = 2300–3900) (Table 1, entries 9–13). For comparison purposes, 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 = 1900–8900; 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

Table 1. Pd-Catalyzed Suzuki Cross-Coupling Polymerization^a



entry	catalyst	base	yield (%) ^b	<i>M</i> _n (PDI) ^c
1	1a	K ₂ CO ₃ (4 equiv)	74	19400 (2.33)
2	1a	Na ₂ CO ₃ (4 equiv)	69	3400 (1.47)
3	1a	KF (4 equiv)	54	2600 (1.28)
4	1a	K ₃ PO ₄ (4 equiv)	85	20100 (2.25)
5	1a	K ₂ HPO ₄ (4 equiv)	75	19000 (2.23)
6	1a	K ₃ PO ₄ (2 equiv)	50	2100 (1.28)
7	1a	K ₃ PO ₄ (3 equiv)	50	2000 (1.11)
8	1a	K ₃ PO ₄ (6 equiv)	74	18500 (2.37)
9	Pd ₂ (dba) ₃ + <i>t</i> -Bu ₃ P (0.5:2)	K ₃ PO ₄ (4 equiv)	30	2300 (1.05)
10	Pd ₂ (dba) ₃ + <i>t</i> -Bu ₃ P (0.5:1)	K ₃ PO ₄ (4 equiv)	60	3900 (1.48)
11	Pd(<i>t</i> -Bu ₃ P) ₂	K ₃ PO ₄ (4 equiv)	51	2600 (1.22)
12	PhPd(<i>t</i> -Bu ₃ P)Br	K ₃ PO ₄ (4 equiv)	58	2700 (1.27)
13	[<i>t</i> -Bu ₃ PPdBr] ₂	K ₃ PO ₄ (4 equiv)	51	3100 (1.35)
14	1b	K ₃ PO ₄ (4 equiv)	41	2600 (1.14)
15	Pd(PPh ₃) ₄	K ₃ PO ₄ (4 equiv)	32	1200 (1.13)
16	1c	K ₃ PO ₄ (4 equiv)	33	2500 (1.05)
17	1d	K ₃ PO ₄ (4 equiv)	89	8900 (2.42)
18	Pd ₂ (dba) ₃ + Xphos (0.5:2)	K ₃ PO ₄ (4 equiv)	68	2200 (1.46)
19	Pd(OAc) ₂ + Xphos (1:2)	K ₃ PO ₄ (4 equiv)	64	2600 (1.47)
20	Pd ₂ (dba) ₃ + Xphos (0.5:1)	K ₃ PO ₄ (4 equiv)	55	2900 (1.65)
21	Pd(OAc) ₂ + Xphos (1:1)	K ₃ PO ₄ (4 equiv)	72	1900 (1.27)
22	Pd(OAc) ₂ + <i>o</i> -Tol ₃ P (1:1)	K ₃ PO ₄ (4 equiv)	64	2900 (1.41)
23	Pd(OAc) ₂ + <i>o</i> -Tol ₃ P (1:2)	K ₃ PO ₄ (4 equiv)	69	2500 (1.29)

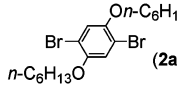
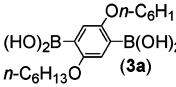
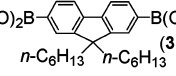
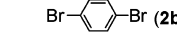
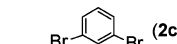
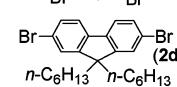
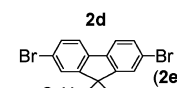
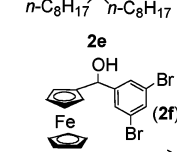
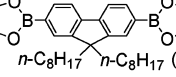
^aPolymerization condition: diboronate (1 equiv), dibromide (1.02 equiv), Pd catalyst (2 mol %), base (1–4 equiv), THF, 60 °C, 1 h. ^bIsolated yield. ^cGPC analysis (polystyrene as standard, THF, 40 °C).

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 arylboronic 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 h or longer for polymerization processes catalyzed by other Pd catalysts (Table 2, entries 1–10). For direct comparison purposes, the Suzuki cross-coupling polymerization of (3,5-

Table 2. Palladacycle Complex **1a-Catalyzed Suzuki Cross-Coupling Polymerization of Aryl Dibromides with Aryldiboronic Acids^a**

$$\text{Br-Ar-Br} + (\text{HO})_2\text{B-Ar'-B(OH)}_2 \xrightarrow[\text{K}_3\text{PO}_4, \text{THF}, 60^\circ\text{C}, 1\text{ h}]{2\text{ mol}\% \text{ 1a}} \left[\text{Ar-Ar}' \right]_n$$

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
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)

^aPolymerization condition: dibromide (1.02 equiv), diboronic acid (1 equiv), Pd catalyst (2 mol %), K₃PO₄ (4 equiv), THF, 60 °C, 1 h. ^bIsolated yields. ^cGPC analysis (polystyrene as standard, THF, 40 °C; average of two runs). ^dReaction time: 20 min. ^eReaction time: 2 h.

dibromophenyl)ferrocenylmethanol (**2f**) with 2,5-dihydroxy-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 = 8200 (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 = 2800 under the condition of refluxing 24 h in THF–H₂O.^{3f} **1a**-Catalyzed polymerization of **2e** with **3b** produced the polymer with a molecular weight of M_n = 82900 (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 h).^{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-phenylamine-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 h 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 toward these directions is currently under way.

■ ASSOCIATED CONTENT

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>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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

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