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Orthoplatinated Triarylphosphite as a Highly Efficient Catalyst for Addition Reactions of Arylboronic Acids with Aldehydes: Low Catalyst Loading Catalysis and a New Tandem Reaction Sequence

Yuan-Xi Liao, Chun-Hui Xing, Ping He, 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

qiaohu@mail.csi.cuny.edu

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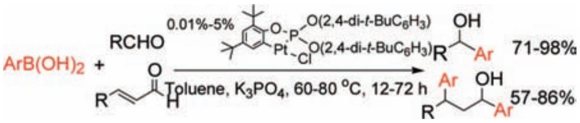
ABSTRACT



Readily available, air/moisture-stable orthoplatinated triarylphosphite catalyzes the addition reactions of arylboronic acids with aldehydes with the catalyst loading as low as 0.01%. It also cataylzes a new tandem reaction of arylboronic acids with α,β-unsaturated aldehydes to form 1,3-diaryl-1-propanols. Our study provides a new paradigm for the application of orthoplatinated triarylphosphites, and may pave the road to develop other Pt(II) catalysts for such addition reactions and other tandem reactions with such addition reactions as part of the reaction sequence.

Over the past decade, transition metal-catalyzed addition reactions of arylboronic acids with aldehydes/ketones have emerged as attractive tools for alcohol synthesis. Rh(I)/ligand complexes,[1–3] Pd(II)/ligand and Pd(0)/$CHCl_3$ complexes,[4] Ni$(COD)_2$/ligands,[5] and CuF_2/(*R*)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole/additive[6] have been reported to be active catalysts for such transformations. Although enormous success, including promising enantioselectivity, has been achieved, drawbacks, e.g., high catalyst loading (3% or more), remain. It is also of great synthetic interest to explore whether transition metal-catalyzed addition reactions of arylboronic acids with alde-

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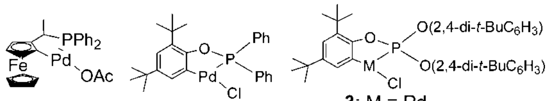
(1) For recent reviews on Rh(I)-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds, see: (a) Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364–3366. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829–2844. (c) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169–196.

(2) For Rh(I)-catalyzed 1,2-addition of arylboronic acids with aldehydes, see: (a) Gois, P. M. P.; Trindade, A. F.; Veiros, L. F.; Andre, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5750–5753. (b) Jagt, R. B. C.; Toullec, P. Y.; Schudde, E. P.; De Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *J. Comb. Chem.* **2007**, *9*, 407–414. (c) Kilincarslan, R.; Yigit, M.; Ozdemir, I.; Cetinkaya, E.; Cetinkaya, B. J. *Heterocycl. Chem.* **2007**, *44*, 69–73. (d) Arao, T.; Suzuki, K.; Kondo, K.; Aoyama, T. *Synthesis* **2006**, 3809–3814. (e) Yan, C.; Zeng, X.; Zhang, W.; Luo, M. *J. Organomet. Chem.* **2006**, *691*, 3391–3396. (f) Suzuki, K.; Ishii, S.; Kondo, K.; Aoyama, T. *Synlett* **2006**, 648–650. (g) Ozdemir, I.; Yigit, M.; Cetinkaya, E.; Cetinkaya, B. *Heterocycles* **2006**, *68*, 1371–1379. (h) Suzuki, K.; Kondo, K.; Aoyama, T. *Synthesis* **2006**, 1360–1364. (i) Duan, H. F.; Xie, J.-H.; Shi, W.-J.; Zhang, Q.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 1479–1481. (j) Jagt, R. B. C.; Toullec, P. Y.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Org. Biomol. Chem.* **2006**, *4*, 773–775. (k) Chen, J.; Zhang, X.; Feng, Q.; Luo, M. *J. Organomet. Chem.* **2006**, *691*, 470–474. (l) Oezdemir, I.; Guerbuez, N.; Seckin, T.; Cetinkaya, B. *Heteroatom Chem.* **2005**, *16*, 461–465. (m) Yigit, M.; Ozdemir, I.; Cetinkaya, E.; Cetinkaya, B. *Appl. Organomet. Chem.* **2005**, *19*, 633–638. (n) Oezdemir, I.; Guerbuez, N.; Goek, Y.; Cetinkaya, B.; Cetinkaya, E. *Transition Metal Chem.* **2005**, *30*, 367–371. (o) Son, S. U.; Kim, S. B.; Reingold, J. A.; Carpenter, G. B.; Sweigart, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 12238–12239. (p) Zhang, W.; Qin, Y.; Zhang, S.; Luo, M. *ARKIVOC* **2005**, *14*, 39–48. (q) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429–436. (r) Huang, R.; Shaughnessy, K. H. *Chem. Commun.* **2005**, 4484–4486. (s) Ozdemir, I.; Demir, S.; Cetinkaya, B. *J. Mol. Catal. A: Chem.* **2004**, *215*, 45–48. (t) Imlinger, N.; Mayr, M.; Wang, D.; Wurst, K.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2004**, *346*, 1836–1843. (u) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957–6960. (v) Pourbaix, C.; Carreaux, F.; Carboni, B. *Org. Lett.* **2001**, *3*, 803–805. (w) Furstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343–350. (x) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450–4452. (y) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683–1686. (z) Aakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 3279–3281.

10.1021/ol800774c CCC: $40.75

hydes/ketones could be combined with other carbon−carbon bond forming reactions into a tandem fashion, a possibility that could make these addtion reactions synthetically more powerful. In this Letter, we report the first Pt-catalyzed addition reactions of arylboronic acids with aldehydes, with very low catalyst loading and a new tandem reaction sequence of arylboronic acids with α,*β*-unsaturated aldehydes.

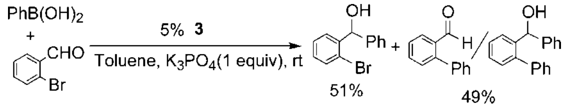
We have recently documented palladacycles **1**−**3** (Figure 1) as highly active catalysts for the addition reaction of arylboronic acids with carbonyl-containing compounds.[7–9] During this study, we observed that the palladacycle **3**-catalyzed addition reaction of phenylboronic acid with 2-bromobenzaldehyde yielded a significant amount of coupling reaction product (Scheme 1). Such an observation suggested that the reductive elimination to generate Pd(0) species, a side reaction that should be responsible for the catalyst decomposition, occurred in palladacycle **3**-catalyzed addition reactions. We thus surmised that minimizing such reductive elimination might be the key to develop highly efficient catalysts with low catalyst loadings.



1 **2** **3**: M = Pd **4**: M = Pt

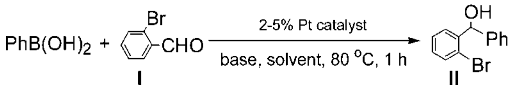
Figure 1.

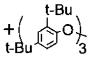
Scheme 1. Palladacycle **3**-Catalyzed Addition Reaction of Phenylboronic Acid with 2-Bromobenzaldehyde



Careful examination of recent studies suggested Pt complexes could be the catalysts with minimized reductive elimination side reaction because diorgano Pt complexes have been demonstrated to undergo reductive elimination very reluctantly, even at elevated temperature.[10,11] Our study thus began with the testing of several Pt complexes for the addition reaction of phenylboronic acid with 2-bromobenzaldehyde. We found that although low efficiency was observed for Pt(COD)Cl_2, Pt(COD)Cl_2 + PPh_3, Pt(COD)Cl_2 + PCy_3, or Pt(COD)Cl_2 + P(2,4-di-*t*-Bu$C_6H_3O)_3$ (Table 1, entries 1−4), readily available orthoplatinated triarylphosphite **4**[10] exhibited promising catalytic activity, especially at higher temperature (Table 1, entries 5 and 6), with no cross-coupling product being observed. These results suggested that with **4** as catalyst, reductive elimination likely did not occur at room temperature or at 80 °C, consistent with previously reported cross-coupling studies.[9,10] Further

Table 1. Platinum-catalyzed Addition Reactions of Phenylboronic Acid with 2-Bromobenzaldehyde



entry	Pt catalyst	solvent	base	ratio of **I** : **II** (%)[b,c]
1	Pt(COD)Cl_2	Toluene	K_3PO_4	>99 : <1
2	Pt(COD)Cl_2 + PPh_3	Toluene	K_3PO_4	95 : 5
3	Pt(COD)Cl_2 + PCy_3	Toluene	K_3PO_4	96 : 4
4	Pt(COD)Cl_2 + ()$_3$P	Toluene	K_3PO_4	>99 : <1
5	**4**	Toluene	K_3PO_4	45 : 55[d]
6	**4**	Toluene	K_3PO_4	1 : 99
7	**4**	THF	K_3PO_4	12 : 88
8	**4**	Dioxane	K_3PO_4	18.5 : 81.5
9	**4**	CH_2Cl_2	K_3PO_4	11: 89
10	**4**	Toluene	K_2CO_3	1.5 : 98.5
11	**4**	Toluene	KOH	22: 78
12	**4**	Toluene	Na_2CO_3	80 : 20
13	**4**	Toluene	Cs_2CO_3	43: 57

[a] Reaction conditions: aldehyde (1.0 equiv), phenylboronic acid (1.5 equiv), solvent (2 mL), base (1−3 equiv), 80 °C. [b] Ratio based on ^{1}H NMR. [c] Cross-coupling product was not observed from ^{1}H NMR. [d] Reaction was carried out at room temperature.

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(3) (a) Toullec, P. Y.; Jagt, R. B. C.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Org. Lett.* **2006**, *8*, 2715–2718. (b) Shintani, R.; Inoue, M.; Hayashi, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3353–3356. (c) Miyamura, S.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 2255–2257.

(4) For Pd(OAc)$_2$/ligand- or cationic Pd(II)-catalyzed 1,2-addition of arylboronic acids with aldehydes, see: (a) Novodomska, A.; Dudicova, M.; Leroux, F. R.; Colobert, F. *Tetrahedron: Asymmetry* **2007**, *18*, 1628–1634. (b) Lin, S.; Lu, X. *J. Org. Chem.* **2007**, *72*, 9757–9760. (c) Qin, C.; Wu, H.; Cheng, J.; Chen, X.; Liu, M.; Zhang, W.; Su, W.; Ding, J. *J. Org. Chem.* **2007**, *72*, 4102–4107. (d) Suzuki, K.; Arao, T.; Ishii, S.; Maeda, Y.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2006**, *47*, 5789–5792. For the Pd(0)/PPh_3/$CHCl_3$ catalyst system, see: (e) Yamamoto, T.; Ohta, T.; Ito, Y. *Org. Lett.* **2005**, *7*, 4153–4155. For an intramolecular addition of arylboronic acids to ketones, see: (f) Liu, G.; Lu, X. *J. Am. Chem. Soc.* **2006**, *128*, 16504–16505.

(5) (a) Arao, T.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2007**, *48*, 4115–4117 (b) Takahashi, G.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y.; Ishikawa, T. *Chem. Commun.* **2005**, 1459–1461. (c) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689–4691.

(6) Tomita, D.; Kanai, D.; Shibasaki, M. *Chem. Asian J.* **2006**, *1*, 161–166.

(7) (a) He, P.; Lu, Y.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 343–346. (b) He, P.; Lu, Y.; Hu, Q.-S. *Tetrahedron. Lett.* **2007**, *48*, 5283–5288.

(8) For the Pd-catalyzed 1,2-addition reaction of arylboronic acids with aldehydes as side reactions to cross-couplings, see: (a) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779–780. (b) Nguyen, H. N.; Huang, X.; Stephen, L.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818–11819.

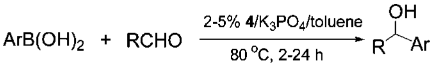
(9) (a) After about 5 months of the appearance of our report on the use of palladacycles **2** and **3** as catalysts for the addition reaction of arylboronic acid with α,*β*-unsaturated ketones, aldehydes, α-keto esters and imines (ref 7b), Bedford et al reported the use of **2** and **3** as catalysts for the addition of arylboronic acids/arylsilanes with enones: Bedford, R. B.; Betham, M.; Charmant, J. P. H.; Haddow, M. F.; Orpen, A. G.; Pilarski, L. T.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2007**, *26*, 6346–6353.

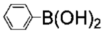
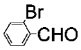
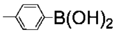
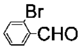
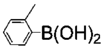
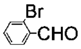
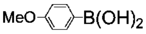
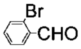
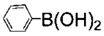
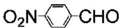
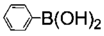
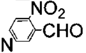
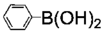
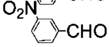
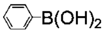
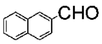
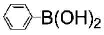
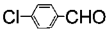
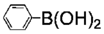
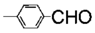
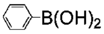
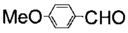
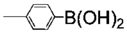
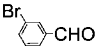
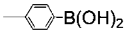
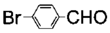
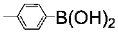
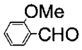
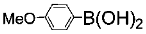
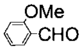
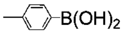
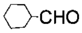
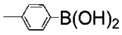
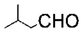
(10) For recent examples see: (a) Pantcheva, I.; Osakada, K. *Organometallics* **2006**, *25*, 1735–1741. (b) Suzuki, Y.; Osakada, K. *Organometallics* **2006**, *25*, 3251–3258. (c) Pantcheva, I.; Nishihara, Y.; Osakada, K. *Organometallics* **2005**, *24*, 3815–3817. (d) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972–2978.

study revealed that toluene was the best solvent and K_3PO_4 and K_2CO_3 the best bases (Table 1, entries 5−13).

With toluene as solvent and K_3PO_4 as base, we employed **4** as catalyst for the addition reactions of a number of aldehydes and arylboronic acids, and our results are listed in Table 2. We found that **4** was a highly efficient, general catalyst. Different arylboronic acids and aromatic aldehydes including activated and deactivated ones (Table 2, entries 1−15) and aliphatic ones (Table 2, entries 16−17) were suitable reagents/substrates for the addition reaction, and high yields were obtained for all cases.

Table 2. Orthoplatinated Triarylphosphite **4**-Catalyzed Addition Reactions of Arylboronic Acids with Aldehydes[a]

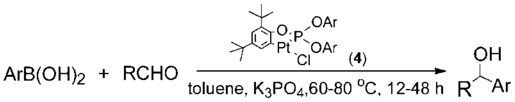


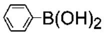
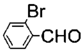
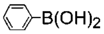
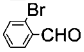
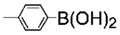
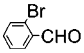
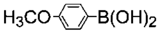
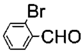
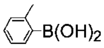
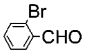
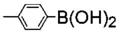
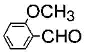
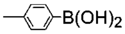
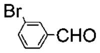
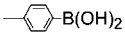
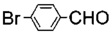
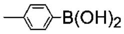
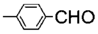
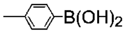
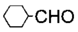
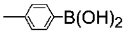
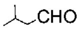
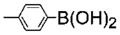
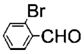
entry	ArB(OH)$_2$	RCHO	yield(%)[b]
1			95
2			91
3			86
4			93
5			96
6			92
7			98
8			85
9			80
10			89
11			87
12			83
13			86
14			83
15			80
16			79
17			78

[a] Reaction conditions: aldehyde (1.0 equiv), arylboronic acid (1.5 equiv), **4** (2−5%), toluene (2 mL), K_3PO_4 (1.0 equiv), room temperature. [b] Isolated yields.

Having confirmed the reluctance of reductive elimination of diorgano Pt complexes generated from orthoplatinated triarylphosphite **4** (Table 1, entries 6−13), which suggested the catalyst decomposition would be minimized, raised the possibility of low catalyst loading catalysis. We tested such a possibility, and our results are listed in Table 3. We found good to excellent yields were obtained in general for all aldehydes and arylboronic acids we tested with the catalyst loading of 0.05−0.1%. We also tested the reaction with the catalyst loading as low as 0.01%, and a good yield of the addition product was obtained (Table 3, entry 12), although a longer reaction time was needed. The similar reaction yields observed with 0.05% and 0.01% catalyst loadings (Table 3, entries 3 and 12) suggested the reductive elimination most likely did not occur, and implied the catalyst loading could potentially be further lowered. To our knowledge, the lowest catalyst loading to obtain a good isolated yield in this field

Table 3. Orthoplatinated Triarylphosphite **4**-Catalyzed Addition Reactions with Low Catalyst Loading[a]



entry	ArB(OH)$_2$	RCHO	cat. loading (%)	yield (%)[b]
1			0.1	90
2			0.05	80
3			0.05	85
4			0.05	86
5			0.05	87
6			0.1	75
7			0.05	84
8			0.05	82
9			0.1	71
10			0.1	72
11			0.1	74
12			0.01	81[c]

[a] Reaction conditions: aldehyde (1.0 equiv), arylboronic acid (1.5 equiv), toluene (2 mL), K_3PO_4 (1.0−3.0 equiv), 60−80 °C. [b] Isolated yields. [c] Reaction time: 72 h.

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(11) For Pt-catalyzed cross-coupling reactions, see: (a) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles, S. J.; Hursthouse, M. B. *Chem. Eur. J.* **2003**, 93216−3227. (b) Bedford, R. B.; Hazelwood, S. L.; Albisson, D. A. *Organometallics* **2002**, *21*, 2599–2600.

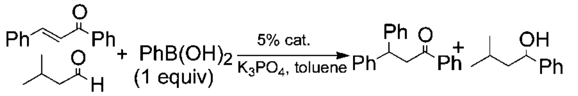
(12) Just before the submission of our manuscript, Kuriyama and coworker reported the Pd/*N*-heterocyclic imidazolium salt-catalyzed addition reaction of phenylboronic acid with benzaldehyde with 0.05% catalyst loading in 99% yield. Further decreasing the catalyst loading led to a significant yield drop (54%), suggesting the catalyst decomposition likely occurred through reductive elimination to prevent the reaction from completion. See: Kuriyama, M.; Shimazawa, R.; Shirai, R. *J. Org. Chem.* **2008**, *73*, 1597–1600.

(13) For examples of Pd-catalyzed 1,4-addition of organoboronic acid with α,β-unsaturated ketones, see: (a) Yamamoto, T.; Iizuka, M.; Ohta, T.; Ito, Y. *Chem. Lett.* **2006**, *35*, 198–199. (b) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025–5032. (c) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2005**, *34*, 720–721. (d) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309–5312. (e) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651–9653. (f) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317–4324. (g) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317–4324. (h) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768–2770. (i) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2003**, *32*, 752–753.

was 0.25%.[4b,12] Our 0.01% catalyst loading thus represents an unprecedentedly low amount.

We have also employed **4** as the catalyst for the competitive addition reaction of phenylboronic acid with chalcone and 3-methylbutanal.[13,14] We found that with **4** as the catalyst, the reaction exclusively occurred at the chalcone while with palladacycle **3** as the catalyst an almost 1:1 ratio of 1,4-addition and 1,2-addition products were observed (Scheme 2). Such a chemoselectivity difference could be explained by the fact that platinum is softer than palladium, and the latter can activate the aldehyde carbonyl group better. These results, combined with the results in Table 2 (entries 16 and 17), suggested that **4** could be an excellent catalyst for a new addition reaction sequence of arylboronic acids with α,β-unsaturated aldehydes: 1,4-addition followed by 1,2-addition. We thus also explored such a tandem reaction sequence and our results are listed in Table 4. Our study showed that the tandem reaction occurred smoothly, and double addition products were obtained in good yields. To our knowledge, previously reported addition reactions of arylboronic acids with enals either afforded 1,2-addition product, allylic alcohols, or 1,4-addition product, β-arylated aldehydes;[15,16] our results represent the first examples that arylboronic acids add to α,β-unsaturated aldehydes successively to form 1,3-diaryl-1-propanols.[17]

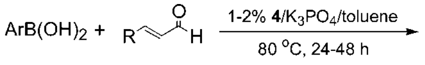
Scheme 2. Cross-Couplings vs. Addition Reactions for Type **I** Palladacycles

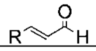
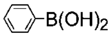
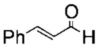
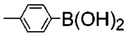
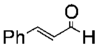
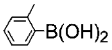
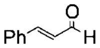
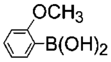
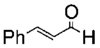
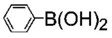
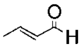


cat.: Palladacycle **3**: room temperature 20 h 55:45
4: 80 °C 20 h >99:1

In summary, we have demonstrated that readily available, air/moisture-stable orthoplatinated triarylphosphite **4** was a highly efficient catalyst for the addition reactions of arylboronic acids with aldehydes, with unprecedentedly low catalyst loading. The soft nature of Pt also allowed us to develop a new tandem reaction sequence of arylboronic acids with α,β-unsaturated aldehydes. The study described here provided a new paradigm for the application of orthoplatinated triarylphosphites,[18,19] and may pave the road for the development of other platinum complexes as unique catalysts for such addition reactions. In addition, our work may also lead to the development of other tandem reactions involving the addition reaction of arylboronic acids with aldehydes as part of the reaction sequence.

Table 4. Tandem Reactions of Arylboronic Acids with Enals Catalyzed by Orthoplatinated Triarylphosphite **4**[a]



entry	ArB(OH)2		yield (%) [b]
1			86
2			80
3			66
4			57
5			63

[a] Reaction conditions: aldehyde (1.0 equiv), aryylboronic acid (3.0 equiv), toluene (2 mL), K_3PO_4 (2.0−6.0 equiv), 80 °C. [b] Isolated yields.

Acknowledgment. We gratefully thank the NSF (CHE0719311) and NIH (GM69704) for funding. Partial support from the PSC-CUNY Research Award Program is also gratefully acknowledged. We also thank Frontier Scientific, Inc. for its generous gifts of arylboronic acids.

Supporting Information Available: General procedures and characterizations of **4**-catalyzed addition reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) For Rh(I)-catalyzed 1,4-addition of organoboronic acid with α,β-unsturated ketones, see reviews: (a) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829–2844. (b) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169–196. Selected recent examples: (c) Trenkle, W. C.; Barkin, J. L.; Son, S. U.; Sweigart, D. A. *Organometallics* **2006**, *25*, 3548–3551. (d) Chen, F.-X.; Kina, A.; Hayashi, T. *Org. Lett.* **2006**, *8*, 341–344. (e) Shintani, R.; Duan, W.-L.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628–5629.

(15) For Rh(I)-catalyzed 1,4-addition reactions of arylboronic acids with enals, see: (a) Douglas, T. M.; Le Notre, J.; Brayshaw, S. K.; Frost, C. G.; Weller, A. S. *Chem. Commun.* **2006**, 3408–3410. (b) Fujita, N.; Motokura, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Jitsukawa, K.; Kaneda, K. *Tetrahedron Lett.* **2006**, *47*, 5083–5087. (c) Trenkle, W. C.; Barkin, J. L.; Son, S. U.; Sweigart, D. A. *Organometallics* **2006**, *25*, 3548–3551. (d) Paquin, J.-F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850–10851. (e) Hayashi, T.; Tokunaga, N.; Okamoto, K.; Shintani, R. *Chem. Lett.* **2005**, *34*, 1480–1481. (f) Itooka, R.; Iguchi, Y.; Miyaura, N. *J. Org. Chem.* **2003**, *68*, 6000–6004. (g) Paquin, F.; Stephenson, C. R. J.; Defieber, C.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 3821–3824. For 1,2-additions, see refs 2i and 2x.

(16) For Pd-catalyzed 1,4-additions of arylboronic acids with enals, see: (a) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Tetrahedron Lett.* **2007**, *48*, 4007–4010. (b) Lin, S.; Lu, X. *Tetrahedron Lett.* **2006**, *47*, 7167–7170. (c) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651–9653. (d) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309–5312. (e) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317–4324. (f) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768–2770.

(17) 1,3-Diaryl-1-propanols are a common structural unit for a number of biologically active compounds or intermediates for the preparation of biologically active compounds. For examples see: (a) Gunn, D.; Akuche, C.; Baryza, J.; Blue, M.-L.; Brennan, C.; Campbell, A.-M.; Choi, S.; Cook, J.; Conrad, P.; Dixon, B.; Dumas, J.; Ehrlich, P.; Gane, T.; Joe, T.; Johnson, J.; Jordan, J.; Kramss, R.; Liu, P.; Levy, J.; Lowe, D.; McAlexander, I.; Natero, R.; Redman, A. M.; Scott, W.; Seng, T.; Sibley, R.; Wang, M.; Wang, Y.; Wood, J.; Zhang, Z. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3053–3057. (b) Boschetti, E.; Molho, D.; Chabert, J.; Grand, M.; Fontaine, L. *Chim. Ther.* **1972**, *7*, 20–23. (c) Skytte, D.; Nielsen, S. F.; Chen, M.; Zhai, L.; Olsen, C. E.; Brogger Christensen, S. *J. Med. Chem.* **2006**, *49*, 436–440.

(18) We found **4** was an excellent catalyst for the 1,4-addition of arylboronic acid with α,β-unsaturated ketones; see the Supporting Information.

(19) The addition of phenylboronic acid with chalcone catalyzed by **4** (5% **4**, room temperature, 1 h, 71% conversion) was recently reported; see ref 9.