ORGANIC LETTERS

2007
Vol. 9, No. 2
343−346

Anionic Four-Electron Donor-Based Palladacycles as Catalysts for Addition Reactions of Arylboronic Acids with α,β-Unsaturated Ketones, Aldehydes, and α-Ketoesters

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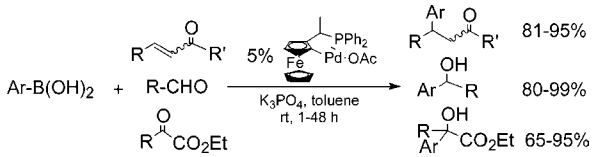
Received November 19, 2006

ABSTRACT



Anionic four-electron donor-based palladacycle-catalyzed 1,4-additions of arylboronic acids with α,β-unsaturated ketones and 1,2-additions of arylboronic acids with aldehydes and α-ketoesters are described. Our study demonstrated that palladacycles were highly efficient, practical catalysts for these addition reactions. The work described here not only opened a new paradigm for the application of palladacycles, but may also pave the road for other metalacycles as practically useful catalysts for such addition reactions including asymmetric ones.

Anionic four-electron donor-based palladacycles, one of the two general types of palladacycles (Figure 1), are readily

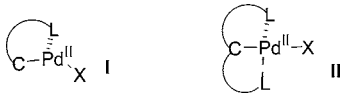


Figure 1. General types of palladacycles.

accessible and air/moisture stable.[1,2] They have been demonstrated as efficient catalyst systems for a number of bond forming reactions including cross-coupling reactions.[1,3] Mechanistic studies suggested that in cross-coupling reactions such as the Suzuki couplings, palladacycles served as the sources of catalytically active species by undergoing transmetalation with organometallic reagents to form transmetalated intermediates such as **A** followed by reductive elimination (Scheme 1). As it has been established that the Pd(II) center in palladacycles could act as a Lewis acid,[1] we reasoned that when carbonyl moieties were present in the reaction system, in addition to undergoing reductive elimination to form Pd-

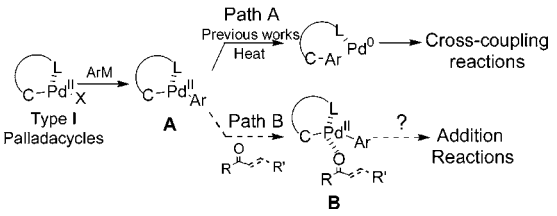
(1) For recent reviews: (a) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527−2572. (b) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055−4082. (c) Bedford, R. B. *Chem. Commun.* **2003**, 1787−1796.

(2) Most Type I palladacycles are known to exist as bridged dimers and to dissociate into monomeric forms during reactions. All Type I palladacycles in this paper were drawn in monomeric forms.

(3) For recent examples: (a) Strieter, E. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 925−928. (b) Moncada, A. I.; Manne, S.; Tanski, J. M.; Slaughter, L. M. *Organometallics* **2006**, *25*, 491−505. (c) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685−692. (d) Consorti, C. S.; Flores, F. R.; Rominger, F.; Dupont, J. *Adv. Synth. Catal.* **2006**, *348*, 133−141. (e) Mino, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191−2194. (f) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685−4696. (g) Rosa, G. R.; Rosa, C. H.; Rominger, F.; Dupont, J.; Monteiro, A. L. *Inorg. Chim. Acta* **2006**, *359*, 1947−1954. (h) Chen, C.-L.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2005**, *24*, 1075−1081.

10.1021/ol062814b CCC: $37.00
Published on Web 12/16/2006

Scheme 1. Cross-Couplings vs Hypothetic Addition Reactions for Type I Palladacycles



(0) species (Path A), **A** might coordinate with a carbonyl moiety to form complexes **B** (Path B) (Scheme 1). On the basis that elevated temperature, typically higher than 100 °C, was required for palladacycles to generate catalytically active species for cross-coupling reactions,[1] we surmised that the reductive elimination of **A** should be slow, especially at lower temperature. We further envisioned that at lower reaction temperature, such as room temperature, **B** might undergo aryl transfer to form addition products much faster than reductive elimination to form cross-coupling products (Scheme 1), and Type I palladacycles could thus catalyze addition reactions of arylboronic acids to carbonyl group-containing compounds,[4−6] a field that is currently dominated by Rh(I) catalysis chemistry.[7−12] The exploration of such palladacycle-catalyzed addition reactions would create a new paradigm for palladacycle catalysis chemistry and may provide powerful catalyst systems for organic synthesis. In this letter, we established that Type I palladacycles could indeed act as efficient catalysts for such addition reactions, specifically, the 1,4-addition of arylboronic acids with α,β-unsaturated ketones and the 1,2-additions of arylboronic acids with aldehydes and α-ketoesters.

We began our study by testing reported palladacycles **1**−**3** for the room temperature 1,4-addition of phenylboronic acid with chalcone, and our results are listed in Table 1. We found

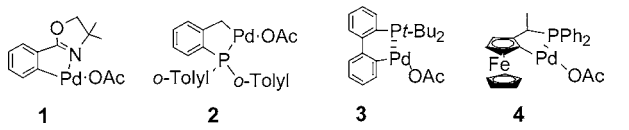


Figure 2. Tested palladacycles.

although palladacycle **1**[13] showed no catalytic activity (Table 1, entry 1), palladacycles **2**[14] and **3**[15] gave encouraging

(4) For palladium-catalyzed 1,4-additions of arylboronic acids with α,β-unsaturated compounds—for Pd(0)/$SbCl_3$ catalyst:Pd(0)/$SbCl_3$ catalyst: (a) Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883−888. For cationic Pd(II) catalysts: (b) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025−5032. (c) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317−4324. Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2005**, *34*, 720−721. (d) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768−2770. For $Pd(OAc)_2$/pyridine catalyst: (e) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651−9653. For $Pd(OCOCF_3)_2$/(*R*,*R*)-Me-Duphos catalyst: (f) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309−5312. For Pd(0)/PPh_3/$CHCl_3$ catalyst: (g) Yamamoto, T.; Iizuka, M.; Ohta, T.; Ito, Y. *Chem. Lett.* **2006**, *35*, 198−199.

(5) (a) For Pd(0)/PPh_3/$CHCl_3$-catalyzed 1,2-addition of arylboronic acids with aldehydes at elevated temperature: Yamamoto, T.; Ohto, T.; Ito, Y. *Org. Lett.* **2005**, *7*, 4153−4155. (b) A 3% yield of 1,2-addition product was observed during the cross-coupling of phenylboronic acid with 3-methoxy-4-tosyloxybenzaldehyde catalyzed by $Pd(OAc)_2$/Buchwald's, biarylphosphine: Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818-1819.

(6) One example of 1,2-addition products of phenylboronic acid with *p*-chlorobenzaldehyde, formed as byproducts during the cross-coupling reaction catalyzed by a palladacycle at 130 °C, was previously reported: Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779−780.

(7) For recent reviews on Rh(I)-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds: (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 and references cited therein.

(8) Selected recent examples of Rh(I)-catalyzed 1,4-additions of arylboronic acids with α,β-unsaturated compounds—with chiral dienes as ligands: (a) Trenkle, W. C.; Barkin, J. L.; Son, S. U.; Sweigart, D. A. *Organometallics* **2006**, *25*, 3548−3551. (b) Chen, F.-X.; Kina, A.; Hayashi, T. *Org. Lett.* **2006**, *8*, 341−344. (c) Shintani, R.; Duan, W.-L.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628−5629. (d) Hayashi, T.; Tokunaga, N.; Okamoto, K.; Shintani, R. *Chem. Lett.* **2005**, *34*, 1480−1481. (e) Paquin, J.-F.; Stephenson, C. R. J.; Defieber, C.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 3821−3824. (f) Shintani R.; Kimura T.; Hayashi T. *Chem. Commun.* **2005**, 3213−3214. (g) Otomaru, Y.; Okamoto, K.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2005**, *70*, 2503−2508. (h) Laeng, F.; Breher, F.; Stein, D.; Gruetzmacher, H. *Organometallics* **2005**, *24*, 2997−3007. (i) Shintani, R.; Okamoto, K.; Hayashi, T. *Org. Lett.* **2005**, *7*, 4757−4759. (j) Otomaru, Y.; Kina, A.; Shintani, R.; Hayashi, T. *Tetrahedron*: *Asymmetry* **2005**, *16*, 1673−1679. (k) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508−11509. With monophosphines and bisphosphines ligands: (l) Vandyck, K.; Matthys, B.; Willen, M.; Robeyns, K.; Van Meervelt, L.; Van der Eycken, J. *Org. Lett.* **2006**, *8*, 363−366. (m) Shimada, T.; Suda, M.; Nagano, T.; Kakiuchi, K. *J. Org. Chem.* **2005**, *70*, 10178−10181. (n) Stemmler, R. T.; Bolm, C. *J. Org. Chem.* **2005**, *70*, 9925−9931. (o) Chen, G.; Tokunaga, N.; Hayashi, T. *Org. Lett.* **2005**, *7*, 2285−2288. (p) Yuan, W.-C.; Cun, L.-F.; Gong, L.-Z.; Mi, A.-Q.; Jiang, Y.-Z. *Tetrahedron Lett.* **2005**, *46*, 509−512. With phosphoramidites as ligands: (q) Mediavilla, U. L.; Krause, N. *Tetrahedron*: *Asymmetry* **2006**, *17*, 494−496. (r) Yamamoto, Y.; Kurihara, K.; Sugishita, N.; Oshita, K.; Piao, D.; Miyaura, N. *Chem. Lett.* **2005**, *34*, 1224−1225. (s) Duursma, A.; Pena, D.; Minnaard, A. J.; Feringa, B. L. *Tetrahedron*: *Asymmetry* **2005**, *16*, 1901−1904. (t) Duursma, A.; Boiteau, J.-G.; Lefort, L.; Boogers, J. A. F.; De Vries, A. H. M.; De Vries, J. G.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2004**, *69*, 8045−8052. With phosphine-olefin bidentate ligands: (u) Shintani, R.; Duan, W.-L.; Nagano, T.; Okada, A.; Hayashi, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4611−4614.

(9) For room temperature Rh(I)-catalyzed 1,2-addition of arylboronic acids with aldehydes: (a) Duan, H.-F.; Xie, J.-H.; Shi, W.-J.; Zhang, Q.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 1479−1481. (b) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450−4452. For Rh(I)-catalyzed addition of arylboronic acids with aldehydes at elevated temperature: (c) Jagt, R. B. C.; Toullec, P. Y; de Vries, J. G.; Feringa, B. L; Minnaard, A. *J. Org. Biomol. Chem.* **2006**, *4*, 773−775. (d) Chen, J.; Zhang, X.; Feng, Q.; Luo, M. *J. Organomet. Chem.* **2006**, *691*, 470−474. (e) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429−436. (f) Ozdemir, I.; Demir, S.; Cetinkaya, B. *J. Mol. Catal. A*: *Chem.* **2004**, *215*, 45−48. (g) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957−6960. (h) Pourbaix, C.; Carreaux, F.; Carboni, B. *Org. Lett.* **2001**, *3*, 803−805. (i) Furstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343−350. (j) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683−1686. (k) Aakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 3279−3281.

(10) (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.

(11) For Rh(I)-catalyzed tandem reactions: (a) Bocknack, B. M.; Wang, L.-C.; Krische, M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5421−5424. (b) Cauble, D. F.; Gipson, J. D.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 1110−1111.

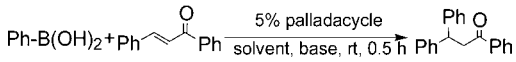
(12) For a report on the Ni-catalyzed addition reaction of arylboronic acids with aldehydes: Takahashi, G.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y.; Ishikawa, T, *Chem. Commun.* **2005**, 1459−1461.

(13) Izumi, T.; Watabe, H.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1711−1714.

(14) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849.

(15) Zim, D.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2413−2415.

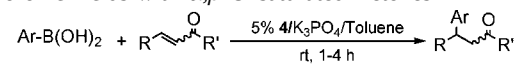
Table 1. Reaction Optimization[a]



entry	palladacycle	solvent	base	conversion (%)[b]
1	**1**	toluene	Cs_2CO_3	0[c]
2	**2**	toluene	Cs_2CO_3	35[c]
3	**3**	toluene	Cs_2CO_3	55[c]
4	**4**	toluene	Cs_2CO_3	95[c]
5	**4**	$ClCH_2CH_2Cl$	K_3PO_4	57
6	**4**	CH_2Cl_2	K_3PO_4	63
7	**4**	THF	K_3PO_4	54
8	**4**	dioxane	K_3PO_4	72
9	**4**	toluene	K_3PO_4	99
10	**4**	toluene	Cs_2CO_3	79
11	**4**	toluene	KF	99
12	**4**	toluene	K_2CO_3	68
13	**4**	toluene	Ag_2CO_3	36

[a] Reaction conditions: chalcone (1.0 equiv), phenylboronic acid (1.5 equiv), solvent (2 mL), base (1 equiv), room temperature. [b] Based on ^1H NMR. [c] Reaction time: 1 h.

Table 2. Palladacycle **4**-Catalyzed Michael Addition of Arylboronic Acids with α,β-Unsaturated Ketones[a]



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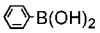
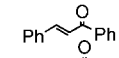
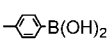
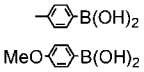
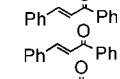
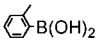
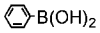
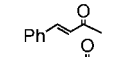
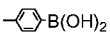
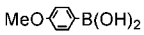
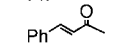
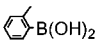
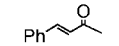
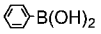
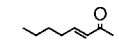
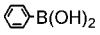
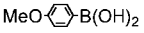
1			95
2			92
3			91
4			94
5			81
6			93
7			93
8			89
9			98
10			90[c]
11			85[c]

[a] Reaction conditions (not optimized): ketone (1.0 equiv), arylboronic acid (1.2−2.0 equiv), **4** (5%), K_3PO_4 (1 equiv), toluene (2 mL), room temperature. [b] Isolated yields (average of two runs). [c] Reaction time: 40 h.

results: 35% conversion was observed for **2** and 55% conversion for **3** (Table 1, entries 2 and 3). It has been established that ArPd(II)R(L_n) complexes with more electron-rich organic groups and/or with less sterically hindered ligands were more reluctant to undergo reductive elimination.[16,17] We reasoned that increasing the electron-richness of the Pd-bonded aromatic part of palladacycles and reducing the size of their ligand part could minimize the reductive elimination and thus might provide more efficient catalysts. We thus prepared ferrocenyl-containing palladacycle **4**.[18] We were pleased to find that **4** was indeed an excellent catalyst for the addition reaction (Table 1, entry 4). We have further employed **4** for the optimization of the reaction condition and our results are also listed in Table 1. We found toluene was the best solvent among the solvents we screened, and K_3PO_4 and KF were the best bases.

With palladacycle **4** as the catalyst, toluene as the solvent, and K_3PO_4 as the base, a number of arylboronic acids and α,β-unsaturated ketones were examined, and our results are listed in Table 2. We found **4** was a robust, general catalyst for the room temperature 1,4-addition of arylboronic acids with α,β-unsaturated ketones including cyclic and acyclic ones (Table 2). The reaction, like other Pd(II)-catalyzed 1,4-addition of arylboronic acids with α,β-unsaturated ketones, most likely involved Pd(II)-enolates as the intermediates, which could undergo reductive elimination to form Heck-type cross-coupling products or protonation to generate the 1,4-addition products.[4] The fact that the Heck coupling products, which are sometimes seen in other Pd(II) catalyst systems,[4] were not detected in ^1H NMR suggested that the reductive elimination process of the Pd(II)-enolate intermediates occurred much slower than that of their protonation process.[19]

We have also employed **4** as the catalyst for the addition reaction of arylboronic acids with aldehydes.[5,6,7,9,12] We were pleased to find that **4** efficiently catalyzed such addition reactions at room temperature (Table 3). Complete conversions and high yields were obtained not only for aromatic aldehydes (Table 3, entries 1−12), but more impressively also for aliphatic aldehydes (Table 3, entries 13 and 14). Since only low yields (≤35%) were observed for room temperature Rh(I)-catalyzed additions of aliphatic aldehydes,[9b] our results suggested that **4** might possess higher catalytic efficiency than reported Rh(I) catalysts.

We have also employed **4** as the catalyst for the addition reaction of arylboronic acids with α-ketoesters, a reaction that could yield useful α-hydroxy esters with an α-quaternary carbon center.[20] Gratifyingly, we found that **4** also efficiently catalyzed such addition reactions at room temperature (Table 4). To our knowledge, these are the first examples of the addition reaction of arylboronic acids with α-ketoesters.[21]

In summary, we have demonstrated that anionic four-electron donor-based, air/moisture stable palladacycle **4** was a highly efficient, robust catalyst for the addition reactions of arylboronic acids with α,β-unsaturated ketones, aldehydes,

(16) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398−3416.

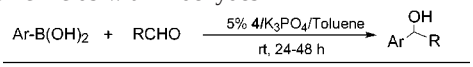
(17) For examples: (a) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866−2873. (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550−9561.

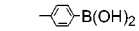
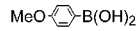
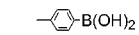
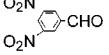
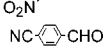
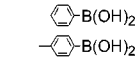
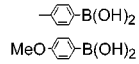
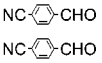
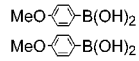
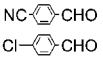
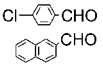
(18) **4** was prepared from ferrocenylmethylphosphine and $Pd(OAc)_2$; for its characterization, see the Supporting Information.

(19) For examples of protonation of palladium(II) enolates see refs 4b and 16. Also see: (a) Hamashima, Y.; Hotta, D.; Sodeoka, M. *J. Am. Chem. Soc.* **2002**, *124*, 11240−11241. (b) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450−5458. (c) Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969−1971.

(20) Coppola, G. M.; Schuster, H. F. *α-Hydroxy Acids in Enantioselective Synthesis*; VCH: Weinhein, Germany, 1997.

Table 3. Palladacycle **4**-Catalyzed Addition Reactions of Arylboronic Acids with Aldehydes[a]



entry	Ar-B(OH)$_2$	RCHO	yield (%) [b]
1			98
2			99
3			94
4			91
5			90
6			95
7			86
8			95
9			98
10			80
11			96
12			91
13			93
14			91
15			89

[a] Reaction conditions (not optimized): aldehyde (1.0 equiv), arylboronic acid (1.2−2.0 equiv), K_3PO_4 (1 equiv), toluene (2 mL), room temperature. [b] Isolated yields (average of two runs).

and α-ketoesters at room temperature. Our study suggested that other readily available and air/moisture stable metalacycles including palladacycles might also be highly efficient, practical catalysts for addition reactions.[22] Our future work will be directed to determine the scope and limitation of metalacycle-including palladacycle-catalyzed addition reactions and to develop the asymmetric version of these processes.

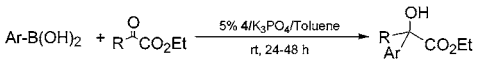
Acknowledgment. We gratefully thank the NIH (GM69704) for funding. Partial support from the PSC-CUNY Research Award Program is also gratefully acknowledged. We also thank Prof. Shi Jin at CSI-CUNY for his help on the solvent purification and Frontier Scientific, Inc. for its generous gifts of arylboronic acids and $Pd(OAc)_2$.

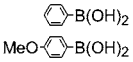
Supporting Information Available: General procedures and characterizations of palladacycle-catalyzed addition reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

OL062814B

(21) (a) For Rh(I)-catalyzed addition of aryltin with α-ketoesters: Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tetrahedron* **2003**, *59*, 4351−4361. For recent examples of dialkylzinc addition of α-ketoesters: (b) Blay, G.; Fernandez, I.; Marco-Aleixandre, A.; Pedro, J. R. *Org. Lett.* **2006**, *8*, 1287−1290. (c) Wieland, L. C.; Deng, H.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 15453−15456. (d) Funabashi, K.; Jachmann, M.; Kanai, M.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5489−5492. (e) DiMauro, E. F.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2002**, *124*, 12668−12669. (f) DiMauro, E. F.; Kozlowski, M. C. *Org. Lett.* **2002**, *4*, 3781−3784.

Table 4. Palladacycle **4**-Catalyzed Addition Reactions of Arylboronic Acids with α-Ketoesters[a]



entry	Ar-B(OH)$_2$	R	yield (%) [b]
1		Ph	94
2		Ph	69
3		Ph	95
4		CH_3	70
5		CH_3	65

[a] Reaction conditions (not optimized): α-ketoester (1.0 equiv), arylboronic acid (1.5−2.0 equiv), K_3PO_4 (1 equiv), toluene (2 mL), room temperature. [b] Isolated yields (average of two runs).

(22) For anionic six-electron donor-based (Type II) palladacycle-catalyzed allylic additions of aldehydes and imines: (a) Solin, N.; Wallner, O. A.; Szabo, K. J. *Org. Lett.* **2005**, *7*, 689−691. (b) Solin, N.; Kjellgren, J.; Szabo, K. J. *J. Am. Chem. Soc.* **2004**; *126*, 7026−7033.