

Pd-catalyzed carbonylation for the construction of tertiary and quaternary carbon centers with sp^3 carbon partners†

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The first examples of a Pd-catalyzed carbonylation of aryl boronic acids with sp^3 carbon partners are presented. Various boronic acids were shown to react with 1,3-diester and 1,3-diketones to afford structurally unique carbonyl compounds. By employing 2-substituted 1,3-diester, synthetically-challenging quaternary carbon centres were accessed. In total, 42 examples of aryl carbonyl compounds were prepared in moderate to good yields. The catalytic system features the use of a bidentated phosphine ligand and a relatively low CO pressure (5 atm), providing an easy, alternative method for the preparation of triketones.

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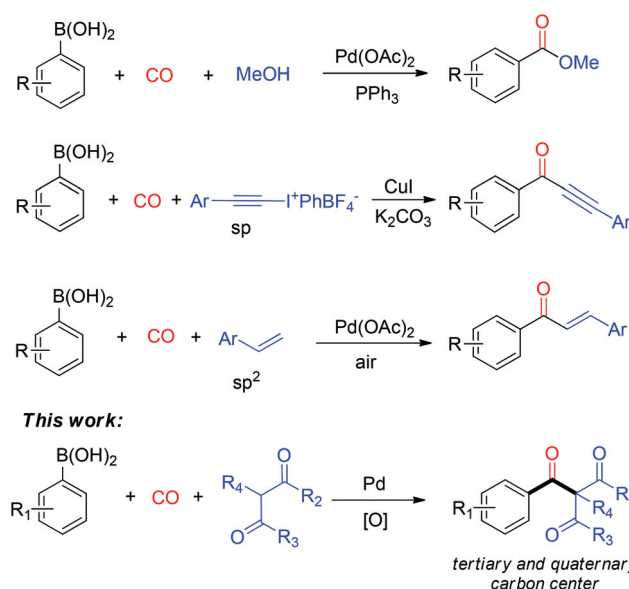
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Introduction

Palladium-catalyzed coupling reactions have become powerful tools for the building of chemical bonds.¹ They are of significant value in a wide range of applications, in particular medical chemicals² and agrochemicals,³ as well as functional materials.⁴ Among the various palladium-catalyzed coupling reactions, carbonylation has been extensively studied.⁵ So far, the carbonylation of aryl halides,^{5a,b,6} triflates,⁷ and tosylates⁸ have all been realized. Examples of carbonylation *via* C–H activation are also emerging.⁹ The most common nucleophilic coupling partners in these reactions are water,^{5l,10} alcohols,^{5k,11} and amines,^{5n,10d,12} which allow for the synthesis of aryl carboxylic acids, esters or amides. The use of carbon-based coupling partners has also been reported. For example, the carbonylative Suzuki reaction couples aryl halides, CO and aryl boronic acids to form aromatic ketones.^{5d,13} Alkenes and alkynes are also viable nucleophiles, as seen in the carbonylative Heck¹⁴ and Sonogashira¹⁵ reactions. All of these carbon nucleophiles contain sp^2 and sp carbon centers. Carbonylation reactions that can accommodate a sp^3 carbon coupling partner, however, are scarce. Although the carbonylation of aryl halides in the presence of malonates was seen early in 1986,¹⁶ only recently was the carbonylation of aryl halides with

ketones and ketone esters as nucleophiles reported by the groups of Skrydstrup and Beller.¹⁷

Aryl boronic acid derivatives are air and moisture stable, and are compatible with a broad range of common functional groups.¹⁸ The carbonylation of aryl boronic acids and derivatives with various coupling partners, including alcohols, alkenes and alkynes, has also been successfully developed (Scheme 1).^{19–21} However, to the best of our knowledge, no examples of the carbonylation of aryl boronic acid with sp^3 carbon partners have been reported yet. Herein, we would like



Scheme 1 The palladium-catalyzed carbonylation of aryl boronic acids with oxygen and carbon nucleophiles.

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to report the first case of an oxidative carbonylation of aryl boronic acids with sp^3 carbon-based nucleophiles, *i.e.* malonates and diketones. The resulting products, triketones, are useful intermediates in organic synthesis, especially for the preparation of biologically active molecules such as phloroglucinols and 5-deazaaminopterin.²²

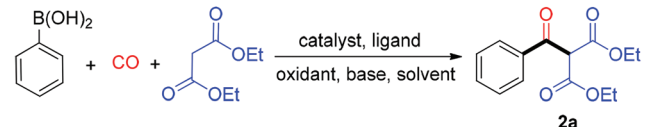
Results and discussion

We set out to examine the Pd-catalyzed carbonylation of phenyl boronic acid with diethyl malonate as the coupling partner (Table 1). The desired product **2a** was obtained in a yield of 16% when catalyzed by $Pd(OAc)_2$ and DPPP in the presence of $AgOAc$ and *t*-BuOLi in MeCN at 80 °C for 12 h (Table 1, entry 1). Control experiments revealed that the metal, ligand, and oxidant were all indispensable for the reaction (Table 1, entries 2–4). Screening of the ligand, solvent and oxidant brought about a better system (Table 1, entries 5–12). Thus, with BINAP as a ligand, Ag_2O as an oxidant and toluene as a solvent, the yield of **2a** was increased to 55% (Table 1, entry 12). Monodentate ligands were inferior. For instance, when using PPh_3 instead of BINAP, the yield dropped to 21%. Further experiments revealed that the catalyst precursors significantly affected the reaction (Table 1, entries 12–14), and it was pleasing that when $Pd(OTFA)_2$ (OTFA: trifluoroacetate) was used as the catalyst, a good yield of 68% was obtained (Table 1, entry 14); this increased to 87% when the concentration of boronic acid was lowered (Table 1, entry 15). Without lowering the concentration, the homo-coupling

product biphenyl was formed in a significant amount. It is also worth noting that when a weaker base, such as Et_3N , was used instead of the *t*-BuOLi, no product could be isolated (Table 1, entry 16).

To explore the scope of the carbonylation reaction, various aryl boronic acids were then examined for coupling with malonates under CO (5 bar), using $Pd(OTFA)_2$ /BINAP as a catalyst and *t*-BuOLi as a base. The results are summarized in Table 2. *para*-Substituted phenyl boronic acids reacted well with diethyl malonate to afford good yields (Table 2, **2b–2i**). No correlation between the electronic properties of the substituents and the reactivity was apparent under the conditions employed. However, lower yields were generally observed for *meta*-substituted substrates, although yields were still acceptable (Table 2, **2j–2l**). As might be expected, *ortho*-substituted boronic acids failed to undergo carbonylation, most likely due to their increased steric demand, which hampers the attack of the nucleophile (see below). Naphthalen-2-ylboronic acid and dimethyl malonate were also viable substrates, albeit ones which showed lower yields (Table 2, **2n, 2o**).


Table 1 Optimization of the reaction conditions^a

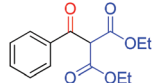
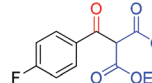
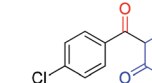
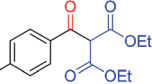
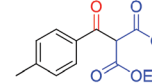
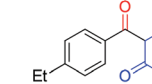
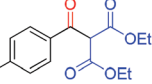
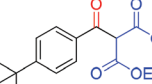
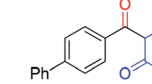
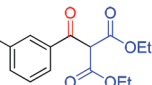
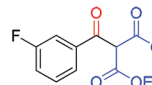
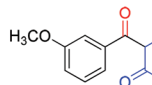
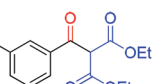
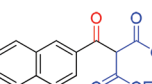
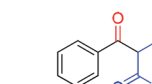


Entry	Catalyst	Ligand	Oxidant	Solvent	Yield ^b (%)
1	$Pd(OAc)_2$	DPPP	$AgOAc$	MeCN	16
2	NO	DPPP	$AgOAc$	MeCN	0
3	$Pd(OAc)_2$	NO	$AgOAc$	MeCN	0
4	$Pd(OAc)_2$	DPPP	NO	MeCN	0
5	$Pd(OAc)_2$	BINAP	$AgOAc$	MeCN	20
6	$Pd(OAc)_2$	DPPE	$AgOAc$	MeCN	Trace
7	$Pd(OAc)_2$	BINAP	$AgOAc$	THF	16
8	$Pd(OAc)_2$	BINAP	$AgOAc$	MePh	49
9	$Pd(OAc)_2$	BINAP	$AgOAc$	Dioxane	10
10	$Pd(OAc)_2$	BINAP	MnO_2	MePh	32
11	$Pd(OAc)_2$	BINAP	$Cu(OAc)_2$	MePh	25
12	$Pd(OAc)_2$	BINAP	Ag_2O	MePh	55
13	$PdCl_2$	BINAP	Ag_2O	MePh	38
14	$Pd(OTFA)_2$	BINAP	Ag_2O	MePh	68
15	$Pd(OTFA)_2$	BINAP	Ag_2O	MePh	87 ^c
16	$Pd(OTFA)_2$	BINAP	Ag_2O	MePh	0 ^d

^a Reaction conditions: aryl boronic acid (0.50 mmol), carbon nucleophile (2 equiv.), CO (5 atm), Pd (5 mol%), ligand (5 mol%), *t*-BuOLi (0.5 mmol), oxidant (2 equiv.), solvent (3 mL), 80 °C, 12 h. ^b Isolated yield. ^c 0.25 mmol of aryl boronic acid. ^d Et_3N was used as a base.

Table 2 The carbonylation of aryl boronic acids with diesters^{a,b}



		
2a, 87%	2b, 82%	2c, 71%
		
2d, 71%	2e, 71%	2f, 76%
		
2g, 81%	2h, 75%	2i, 81%
		
2j, 62%	2k, 68%	2l, 71%
		
2m, 62%	2n, 58%	2o, 52%

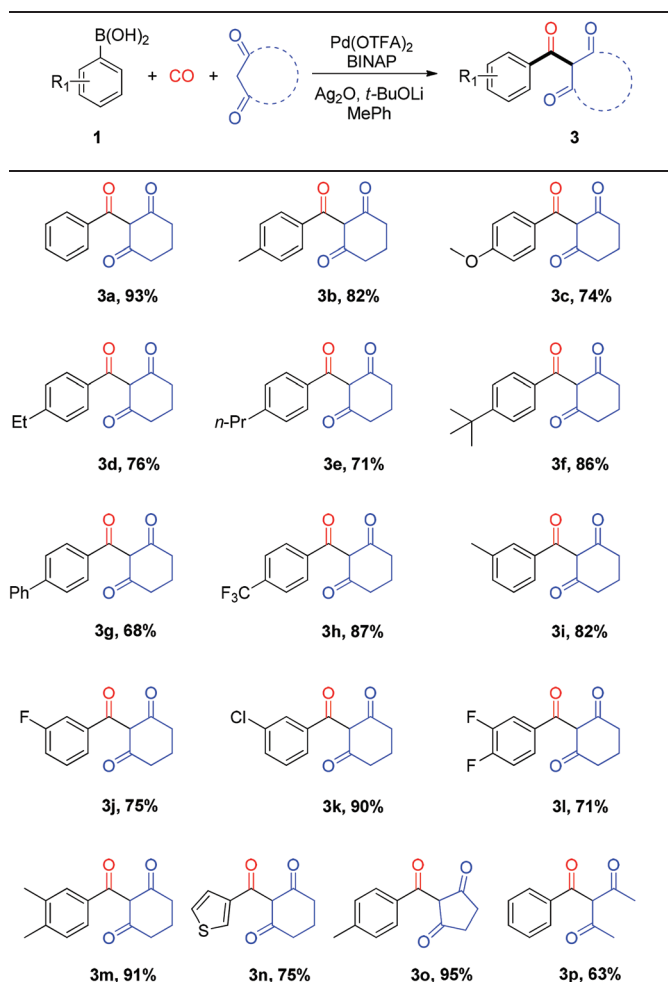
^a Reaction conditions: aryl boronic acid (0.25 mmol), carbon nucleophile (0.5 mmol), CO (5 atm), $Pd(OTFA)_2$ (5 mol%), BINAP (5 mol%), Ag_2O (0.5 mmol), *t*-BuOLi (0.5 mmol), toluene (3 mL), 80 °C, 12 h. ^b Isolated yield given below each product.

Apart from the malonates, 1,3-diketones turned out to be good carbonylation coupling partners with boronic acids. Good to excellent yields were obtained for a range of aryl boronic acids coupled with cyclohexane-1,3-dione (Table 3, **3a–3m**). Compared with the malonates, slightly higher yields were observed for 1,3-diketones in general, presumably reflecting their reduced steric demand. Notably, an excellent yield of 87% was obtained for the very electron deficient *para*-CF₃-phenyl boronic acid (Table 3, **3h**). Interestingly, excellent yields were also obtained for some *meta*-substituted aryl boronic acids (Table 3, **3i**, **3k**). A 75% yield was recorded for thiophen-3-yl boronic acid, showcasing the utility of this method for functionalizing heterocycles (Table 3, **3n**). With cyclopentane-1,3-dione as the nucleophile, a remarkable yield of 95% was produced (Table 3, **3o**). The noncyclic compound, pentane-2,4-dione, also reacted; however, the yield was lower (Table 3, **3p**). These examples lend support to the suggested steric effect. The yields obtained appear to be comparable with those

reported by Skrydstrup and co-workers in the carbonylation of aryl bromides.^{17c}

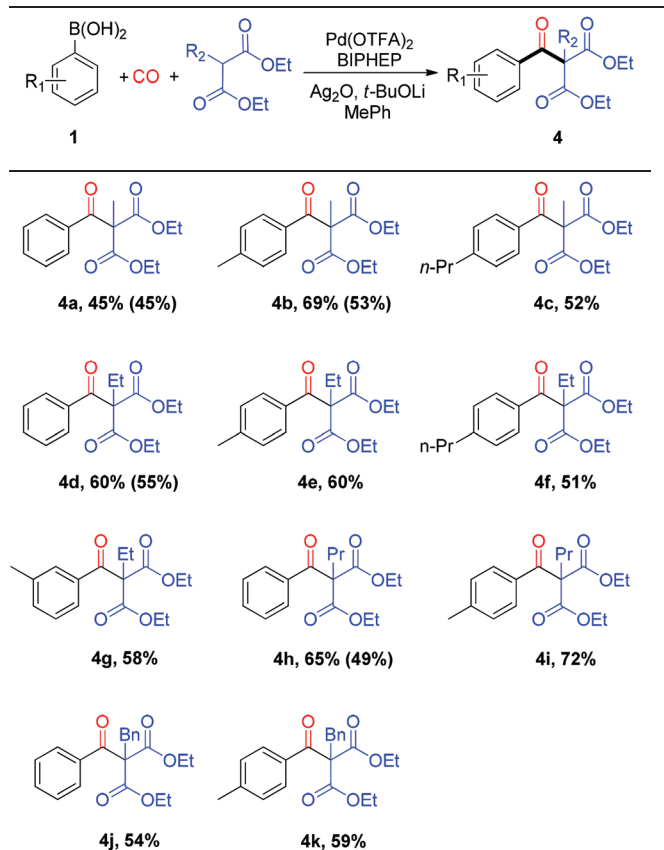
The more challenging carbonylation with 2-substituted 1,3-dicarbonyl compounds, which leads to quaternary carbon centers, was also examined. Using Pd(OTFA)₂/BINAP as a catalyst, the carbonylation was slower than those shown in Table 2, affording unsatisfactory yields in general (Table 4). Considering the possible reaction mechanism (see below), a ligand with a smaller steric bulkiness, 2,2'-bis(diphenylphosphino)-1,1'-biphenyl (BIPHEP), was tested and found to give better yields, although they were still inferior to those given above. As is seen in Table 4, substituents with varying steric hindrances, including methyl, ethyl, propyl and benzyl groups, could all be tolerated. Interestingly, the increase in chain length of the substituents on the malonates even increased the yields of products in some cases (Table 4, **4a**, **4d**, **4h**). Notably, a good yield of 72% was obtained for the reaction of *para*-methylphenyl boronic acid with *n*-propyl substituted diethyl malonate (Table 4, **4i**). These reactions represent the first examples of

Table 3 Carbonylation of aryl boronic acids with cyclic diketones^{a,b}



^a Reaction conditions: aryl boronic acid (0.25 mmol), carbon nucleophile (0.5 mmol), CO (5 atm), Pd(OTFA)₂ (5 mol%), BINAP (5 mol%), Ag₂O (0.5 mmol), *t*-BuOLi (0.5 mmol), toluene (3 mL), 80 °C, 12 h. ^b Isolated yield given below each product.

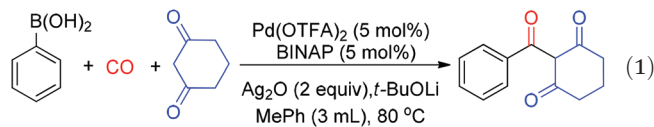
Table 4 Carbonylation of aryl boronic acids with 2-substituted 1,3-diester^{a,b}



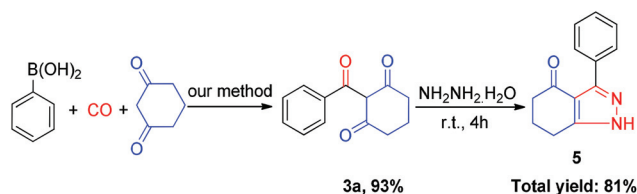
^a Reaction conditions: aryl boronic acid (0.25 mmol), carbon nucleophile (0.5 mmol), CO (5 atm), Pd(OTFA)₂ (10 mol%), BIPHEP (10 mol%), Ag₂O (0.5 mmol), *t*-BuOLi (0.5 mmol), toluene (3 mL), 80 °C, 12 h. ^b Isolated yield given below each product; the number in brackets refers to the yield obtained with BINAP.

carbonylative coupling of boronic acids which form quaternary carbon centers.

To further demonstrate the power of this new synthetic method, the synthesis of an indazole,²³ **5**, was carried out. Using our method as a key step, an 81% yield of **5** was obtained over two steps, starting from simple phenyl boronic acid (Scheme 2). Indazoles are compounds with various bio-activities and **5** is in fact a key intermediate for the synthesis of an antitumour agent.²⁴



To gain insight into the reaction mechanism, the kinetic profiles and the effect of the concentration of the base, as well as the CO pressure, were studied, using the carbonylation of phenyl boronic acid with cyclohexane-1,3-dione as a model reaction under the conditions shown in eqn (1). A steady increase in the yield with time was observed, showing that the carbonylation rate varies with the concentration of the substrate (Fig. 1). The effect of the amount of base was also investigated (Fig. 2). Interestingly, at 1 bar of CO pressure, the reaction rate was not significantly affected by the base concentration; whilst at 5 bar of CO pressure, an increase in the amount of base led to faster reaction rates. Since the concentration of the nucleophile, *i.e.* the enolate derived from the diketone, is directly proportional to that of the base, the observed effect of the base concentration seems to suggest that



Scheme 2 The carbonylation-enabled synthesis of an indazole.

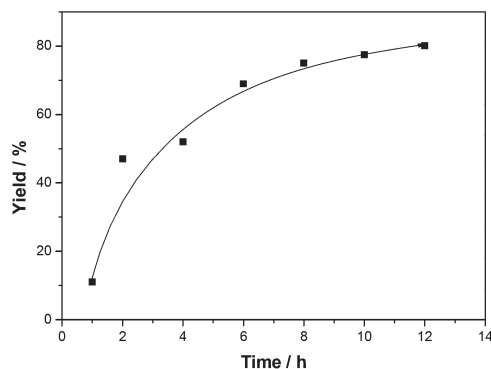


Fig. 1 Variation of the yield with time in the carbonylation of phenyl boronic acid. Conditions: phenyl boronic acid (0.25 mmol), 1,3-diketone (0.5 mmol), Pd(OTFA)₂ (5 mol%), BINAP (5 mol%), CO (5 bar), *t*-BuOLi (0.5 mmol), Ag₂O (0.5 mmol), 80 °C, in toluene (3 mL).

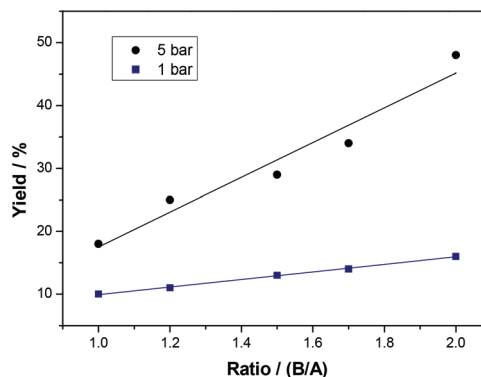


Fig. 2 Variation of the yield with the amount of base in the carbonylation of phenyl boronic acid. Conditions (B/A, molar ratio of base: boronic acid): phenyl boronic acid (0.25 mmol), 1,3-diketone (0.5 mmol), Pd(OTFA)₂ (5 mol%), BINAP (5 mol%), CO (1 or 5 bar), *t*-BuOLi, Ag₂O (0.5 mmol), 80 °C, 10 h, in toluene (3 mL).

at a high CO pressure, the reaction rate is determined by the step that involves the enolate; whilst at a low CO pressure, the CO concentration affects the reaction rate. This hypothesis is further supported by the effect of the CO pressure observed (Fig. 3).

A volcano-shaped curve was obtained for the variation of yields with the pressure of CO (Fig. 3). The highest yield was obtained at 5 bar of CO. At pressures lower than 5 bar, the reaction rate increased with an increase in CO pressure, indicating that the diffusion of CO gas into the solution may limit the reaction rate. The decrease in the rate at higher than 5 bar CO pressure may stem from the faster reduction of Pd(II) to Pd(0) by CO, which would slow down the transmetalation of boronic acid to Pd(II).²⁵ Alternatively, catalytically inactive palladium carbonyl species may be formed under a high CO pressure.²⁶ Without CO, however, homo-coupled biphenyl and phenol were obtained as the major products, indicating that the transmetalation process easily occurs. This result, together with the fact that homo-coupling and deboration products

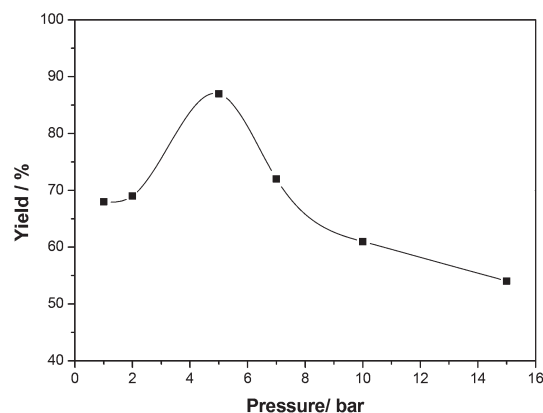
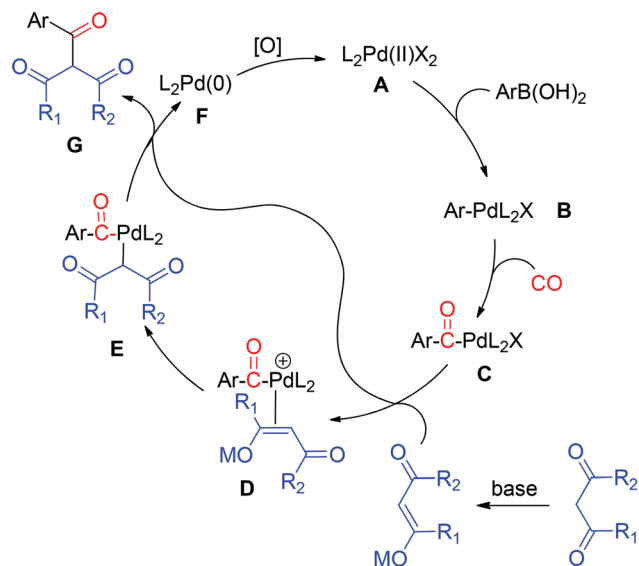


Fig. 3 Variation of the yield with CO pressure in the carbonylation of phenyl boronic acid. Conditions: phenyl boronic acid (0.25 mmol), 1,3-diketone (0.5 mmol), Pd(OTFA)₂ (5 mol%), BINAP (5 mol%), CO, *t*-BuOLi (0.5 mmol), Ag₂O (0.5 mmol), 80 °C, 10 h, in toluene (3 mL).



Scheme 3 A proposed mechanism for the carbonylation of boronic acid featuring a sp^3 carbon nucleophile.

were not observed in the presence of CO, suggests that CO insertion is also a relatively fast process.

A suggested mechanism is presented in Scheme 3.²⁷ The transmetalation of aryl boronic acid with a Pd(II) complex, **A**, produces the intermediate **B**, which undergoes CO insertion to afford the Pd-acyl complex **C**. The enolate then coordinates to the Pd center to form the intermediate **D**, which isomerizes to **E**. **E** could also be formed *via* a palladium-enolate species without going through **D**.²⁸ Product **G** is released through reductive elimination, generating the Pd(0) species **F**, the oxidation of which regenerates the active catalyst **A**. Alternatively, a direct nucleophilic attack by the enolate at the Pd-acyl may take place, affording **G** and **F**. The results above do not allow these two pathways to be discerned, however.

Conclusions

In conclusion, we have developed the first carbonylation of aryl boronic acids with sp^3 carbon coupling partners. The catalytic system demonstrates a broad substrate scope, allowing for the carbonylation of various aryl boronic acids with malonates or 1,3-diketones to afford tertiary and, more remarkably, quaternary carbon centers. Whilst preliminary studies indicate that the carbonylation turnover is limited by the nucleophilic attack or reductive elimination steps, details of the reaction mechanism remain to be delineated.

Experimental section

General methods

Flash chromatography was performed with freshly distilled solvents. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using CDCl_3 as a solvent. Chemical shifts (δ) are

reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Toluene was dried over sodium for 4 h, and distilled under N_2 atmosphere.

Procedure for preparation of diethyl 2-benzoylmalonate

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. *t*-BuOLi (0.5 mmol) and carbon nucleophiles (0.5 mmol) were placed in a 10 mL Teflon reaction tube and then solvent (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, a Pd catalyst (0.025 mmol), a ligand (0.025 mmol), aryl boronic acid (0.25 mmol) and an oxidant (0.5 mmol) were added to the tube, to which was added 2 mL solvent with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 80 °C for 12 h. The autoclave was then cooled to room temperature and vented, to discharge the excess CO in the fume hood. Water (10 mL) was added, and the product was extracted with ethyl acetate (3×15 mL). The organic layers were washed with brine, dried over Na_2SO_4 , and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as an eluent, to give the carbonylation product.

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Notes and references

- (a) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483; (b) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461–1473.
- R. Hersperger, K. Bray-French, L. Mazzoni and T. Müller, *J. Med. Chem.*, 2000, **43**, 675–682.
- D. Angeles-Wedler, K. Mackenzie and F.-D. Kopinke, *Environ. Sci. Technol.*, 2008, **42**, 5734–5739.
- M. E. Wright and S. R. Pulley, *Macromolecules*, 1989, **22**, 2542–2544.
- (a) A. Schoenberg, I. Bartoletti and R. F. Heck, *J. Org. Chem.*, 1974, **39**, 3318–3326; (b) A. Schoenberg and R. F. Heck, *J. Am. Chem. Soc.*, 1974, **96**, 7761–7764; (c) M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17–85; (d) J. J. Brunet and R. Chauvin, *Chem. Soc. Rev.*, 1995, **24**, 89–95; (e) C. Coperet, T. Sugihara, G. Wu,

- I. Shimoyama and E.-i. Negishi, *J. Am. Chem. Soc.*, 1995, **117**, 3422–3431; (f) I. Pri-Bar and J. Schwartz, *J. Org. Chem.*, 1995, **60**, 8124–8125; (g) F. Paul, J. Fischer, P. Ochsenbein and J. A. Osborn, *Organometallics*, 1998, **17**, 2199–2206; (h) M. M. Bio and J. L. Leighton, *Org. Lett.*, 2000, **2**, 2905–2907; (i) O. Hamed, A. El-Qisairi and P. M. Henry, *Tetrahedron Lett.*, 2000, **41**, 3021–3024; (j) K. Ueda, Y. Sato and M. Mori, *J. Am. Chem. Soc.*, 2000, **122**, 10722–10723; (k) E. Mizushima, T. Hayashi and M. Tanaka, *Green Chem.*, 2001, **3**, 76–79; (l) V. Calò, P. Giannoccaro, A. Nacci and A. Monopoli, *J. Organomet. Chem.*, 2002, **645**, 152–157; (m) A. Kamitani, N. Chatani and S. Murai, *Angew. Chem., Int. Ed.*, 2003, **42**, 1397–1399; (n) K. Kumar, A. Zapf, D. Michalik, A. Tillack, T. Heinrich, H. Böttcher, M. Arlt and M. Beller, *Org. Lett.*, 2003, **6**, 7–10; (o) R. Skoda-Földes, E. Takacs, J. Horvath, Z. Tuba and L. Kollar, *Green Chem.*, 2003, **5**, 643–645; (p) J.-H. Li, S. Tang and Y.-X. Xie, *J. Org. Chem.*, 2004, **70**, 477–479; (q) M. Yuguchi, M. Tokuda and K. Orito, *J. Org. Chem.*, 2004, **69**, 908–914; (r) Y. Harada, Y. Fukumoto and N. Chatani, *Org. Lett.*, 2005, **7**, 4385–4387; (s) A. Brennfürer, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2009, **48**, 4114–4133; (t) X.-F. Wu, H. Neumann and M. Beller, *Chem. Rev.*, 2012, **113**, 1–35.
- 6 (a) S. Klaus, H. Neumann, A. Zapf, D. Strübing, S. Hübner, J. Almena, T. Riermeier, P. Groß, M. Sarich, W.-R. Krahnert, K. Rossen and M. Beller, *Angew. Chem., Int. Ed.*, 2006, **45**, 154–158; (b) J. R. Martinelli, T. P. Clark, D. A. Watson, R. H. Munday and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2007, **46**, 8460–8463; (c) A. G. Sergeev, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2008, **130**, 15549–15563; (d) X.-F. Wu, L. Wu, R. Jackstell, H. Neumann and M. Beller, *Chem. – Eur. J.*, 2013, **19**, 12245–12248; (e) X.-F. Wu, S. Oschatz, M. Sharif, M. Beller and P. Langer, *Tetrahedron*, 2014, **70**, 23–29.
- 7 (a) X.-F. Wu, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 5284–5288; (b) X.-F. Wu, B. Sundararaju, H. Neumann, P. H. Dixneuf and M. Beller, *Chem. – Eur. J.*, 2011, **17**, 106–110.
- 8 R. H. Munday, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2008, **130**, 2754–2755.
- 9 (a) Y. Lu, D. Leow, X. Wang, K. M. Engle and J.-Q. Yu, *Chem. Sci.*, 2011, **2**, 967–971; (b) H. Zhang, D. Liu, C. Chen, C. Liu and A. Lei, *Chem. – Eur. J.*, 2011, **17**, 9581–9585; (c) R. Lang, L. Shi, D. Li, C. Xia and F. Li, *Org. Lett.*, 2012, **14**, 4130–4133; (d) P. Xie, Y. Xie, B. Qian, H. Zhou, C. Xia and H. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 9902–9905.
- 10 (a) Y. Ben-David, M. Portnoy and D. Milstein, *J. Am. Chem. Soc.*, 1989, **111**, 8742–8744; (b) A. V. Cheprakov, N. V. Ponomareva and I. P. Beletskaya, *J. Organomet. Chem.*, 1995, **486**, 297–300; (c) A. M. Trzeciak and J. J. Ziolkowski, *J. Mol. Catal. A: Chem.*, 2000, **154**, 93–101; (d) J. McNulty, J. J. Nair and A. Robertson, *Org. Lett.*, 2007, **9**, 4575–4578; (e) D. A. Watson, X. Fan and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 7096–7101.
- 11 (a) V. Dufaud, J. Thivolle-Cazat and J.-M. Basset, *J. Chem. Soc., Chem. Commun.*, 1990, 426–427; (b) T. Satoh, K. Kokubo, M. Miura and M. Nomura, *Organometallics*, 1994, **13**, 4431–4436; (c) W. Mägerlein, A. F. Indolese and M. Beller, *Angew. Chem., Int. Ed.*, 2001, **40**, 2856–2859.
- 12 (a) E. Morera and G. Ortar, *Tetrahedron Lett.*, 1998, **39**, 2835–2838; (b) R. Skoda-Földes, Z. Szarka, L. Kollár, Z. Dinya, J. Horváth and Z. Tuba, *J. Org. Chem.*, 1999, **64**, 2134–2136; (c) C. Mingzhong, Z. Jun, Z. Hong and S. Caisheng, *React. Funct. Polym.*, 2002, **50**, 191–195; (d) N. Tsukada, Y. Ohba and Y. Inoue, *J. Organomet. Chem.*, 2003, **687**, 436–443; (e) Y. Li, H. Alper and Z. Yu, *Org. Lett.*, 2006, **8**, 5199–5201; (f) A. C. Tadd, A. Matsuno, M. R. Fielding and M. C. Willis, *Org. Lett.*, 2009, **11**, 583–586; (g) E. J. Yoo, M. Wasa and J.-Q. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 17378–17380; (h) J. E. R. Sadig, R. Foster, F. Wakenhut and M. C. Willis, *J. Org. Chem.*, 2012, **77**, 9473–9486; (i) M. V. Khedkar, T. Sasaki and B. M. Bhanage, *ACS Catal.*, 2013, **3**, 287–293.
- 13 (a) T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki and N. Miyaoura, *J. Org. Chem.*, 1998, **63**, 4726–4731; (b) S. Zheng, L. Xu and C. Xia, *Appl. Organomet. Chem.*, 2007, **21**, 772–776.
- 14 (a) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 14596–14602; (b) X.-F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 14596–14602; (c) X.-F. Wu, H. Jiao, H. Neumann and M. Beller, *ChemCatChem*, 2011, **3**, 726–733; (d) J. Schranck, X.-F. Wu, H. Neumann and M. Beller, *Chem. – Eur. J.*, 2012, **18**, 4827–4831.
- 15 (a) M. S. Mohamed Ahmed and A. Mori, *Org. Lett.*, 2003, **5**, 3057–3060; (b) A. S. Karpov, E. Merkul, F. Rominger and T. J. J. Müller, *Angew. Chem., Int. Ed.*, 2005, **44**, 6951–6956; (c) B. Liang, M. Huang, Z. You, Z. Xiong, K. Lu, R. Fathi, J. Chen and Z. Yang, *J. Org. Chem.*, 2005, **70**, 6097–6100; (d) M. T. Rahman, T. Fukuyama, N. Kamata, M. Sato and I. Ryu, *Chem. Commun.*, 2006, 2236–2238.
- 16 T.-A. Kobayashi and M. Tanaka, *Tetrahedron Lett.*, 1986, **27**, 4745–4748.
- 17 (a) T. M. Gøgsig, R. H. Taaning, A. T. Lindhardt and T. Skrydstrup, *Angew. Chem., Int. Ed.*, 2012, **51**, 798–801; (b) S. Korsager, D. U. Nielsen, R. H. Taaning, A. T. Lindhardt and T. Skrydstrup, *Chem. – Eur. J.*, 2013, **19**, 17687–17691; (c) D. U. Nielsen, C. Lescot, T. M. Gøgsig, A. T. Lindhardt and T. Skrydstrup, *Chem. – Eur. J.*, 2013, **19**, 17926–17938; (d) J. Schranck, A. Tlili, P. G. Alsabeh, H. Neumann, M. Stradiotto and M. Beller, *Chem. – Eur. J.*, 2013, **19**, 17926–17938; (e) X.-F. Wu, H. Neumann and M. Beller, *Chem. Soc. Rev.*, 2011, **40**, 4986–5009.
- 18 (a) A. Suzuki, *Acc. Chem. Res.*, 1982, **15**, 178–184; (b) N. Miyaoura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
- 19 C. S. Cho, T. Ohe and S. Uemura, *J. Organomet. Chem.*, 1995, **496**, 221–226.
- 20 (a) C.-M. Yu, J.-H. Kweon, P.-S. Ho, S.-C. Kang and G. Y. Lee, *Synlett*, 2005, 2631–2634; (b) X.-F. Wu,

- H. Neumann and M. Beller, *Chem. – Asian J.*, 2012, **7**, 282–285.
- 21 (a) Q. Liu, G. Li, J. He, J. Liu, P. Li and A. Lei, *Angew. Chem., Int. Ed.*, 2010, **122**, 3443–3446; (b) Q. Liu, H. Zhang and A. Lei, *Angew. Chem., Int. Ed.*, 2011, **50**, 10788–10799; (c) X.-F. Wu, H. Neumann and M. Beller, *ChemSusChem*, 2013, **6**, 229–241.
- 22 (a) M. E. Y. Francisco, H. H. Seltzman, A. F. Gilliam, R. A. Mitchell, S. L. Rider, R. G. Pertwee, L. A. Stevenson and B. F. Thomas, *J. Med. Chem.*, 2002, **45**, 2708–2719; (b) M. Terada, M. Nakano and H. Ube, *J. Am. Chem. Soc.*, 2006, **128**, 16044–16045.
- 23 A. O. Fitton and R. K. Smalley, *Practical Heterocyclic Chemistry*, Academic Press, New York, 1968.
- 24 P. Barraja, V. Spano, D. Giallombardo, P. Diana, A. Montalbano, A. Carbone, B. Parrino and G. Cirrincione, *Tetrahedron*, 2013, **69**, 6474–6477.
- 25 R. Giri, J. K. Lam and J.-Q. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 686–693.
- 26 T. A. Stromnova and I. I. Moiseev, *Russ. Chem. Soc.*, 1998, **67**, 485–514.
- 27 (a) P. E. Garrou and R. F. Heck, *J. Am. Chem. Soc.*, 1976, **98**, 4115–4127; (b) D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1986, 817–818; (c) F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto and A. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 3235–3245; (d) Y.-S. Lin and A. Yamamoto, *Organometallics*, 1998, **17**, 3466–3478; (e) F. Ozawa, N. Kawasaki, H. Okamoto, T. Yamamoto and A. Yamamoto, *Organometallics*, 1987, **6**, 1640–1651; (f) F. Ozawa, L. Huang and A. Yamamoto, *J. Organomet. Chem.*, 1987, **334**, C9–C13; (g) W. R. Moser, A. W. Wang and N. K. Kildahl, *J. Am. Chem. Soc.*, 1988, **110**, 2816–2820.
- 28 (a) T. Nishikata, Y. Yamamoto and N. Miyaura, *Organometallics*, 2004, **23**, 4317–4324; (b) T. Nishikata, Y. Yamamoto, I. D. Gridnev and N. Miyaura, *Organometallics*, 2005, **24**, 5025–5032.