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Tandem β-Boration/Arylation of α,β-Unsaturated Carbonyl Compounds by Using a Single Palladium Complex To Catalyse Both Steps

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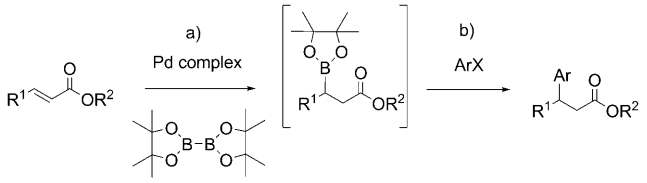
Abstract: Diphenyl(3-methyl-2-indolyl)phosphine ($C_9H_8NPPh_2$, **1**) gives stable dimeric palladium(II) complexes that contain the phosphine in P,N-bridging coordination mode. On treating **1** with $[Pd(O_2CCH_3)_2]$, the new complexes $[Pd(\mu\text{-}C_9H_7NPPh_2)(NCCH_3)]_2$ (**2**) or $[Pd(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCH_3)]_2$ (**3**) were isolated, depending on the solvent used, acetonitrile or toluene, respectively. Further reaction of **3** with the ammonium salt of **1** led to the substitution of one carboxylate ligand to afford $[Pd(\mu\text{-}C_9H_7NPPh_2)_3(\mu\text{-}O_2CCH_3)]$ (**4**), in which the bimetallic unit is bonded by three $C_9H_7NPPh_2^-$ moieties and one carboxylate group. Using this methodology, $[Pd_2(\mu\text{-}C_6H_4PPh_2)_2(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCX_3)]$ (X = H (**7**); X = F (**8**)) were synthesised from the *ortho*-metalated compounds $[Pd(C_6H_4PPh_2)(\mu\text{-}O_2CCX_3)]_2$ (X = H (**5**); X = F (**6**)). Complexes **3**, **4**, **7**, and **8** have been found to be active in the catalytic β-boration of α,β-unsaturated esters and ketones under mild reaction conditions. Hindrance of the carbonyl moiety has an influence on the reaction rate, but quantitative conversion was achieved in many cases. More remarkably, when aryl bromides were added to the reaction media, complex **7** induced a highly successful consecutive β-boration/cross-coupling reaction with dimethyl acrylamide as the substrate (99% conversion, 89% isolated yield).

Keywords: arylation · domino reactions · heterogeneous catalysis · N,P ligands · palladium

Introduction

Electronic directing effects give rise to regioisomeric organoboronate formation in the metal-mediated β-boration of α,β-unsaturated carbonyl substrates (Scheme 1, path a).[1] This functionalisation creates a stereogenic centre at the β-carbon, and enantioselectivity can be induced with an appropriate catalyst.[2] Despite the selectivity of the C–B bond formation and the retention of configuration in the functionalisation process by which the organoborane intermediates are converted to the target products, to the best of our knowledge the oxidation–acylation reaction is the only functionalisation protocol to have been explored so far.[3] We became interested in the selective synthesis of β-boryl esters as a platform for introducing a β-aryl functionality through a subsequent cross-coupling reaction. We also attempted to conduct both catalytic reactions, β-boration followed by arylation, using the same palladium-based catalytic system (Scheme 1).



Scheme 1. a) β-boration, b) arylation.

We were the first to demonstrate that palladium complexes catalyse the diboration reaction of alkenes[4] despite the unfavourable oxidative addition of the diboron reagent to Pd^0.[5] We also proposed the first palladium-mediated β-boration of α,β-unsaturated esters, in which asymmetric induction was achieved in the presence of appropriate chiral

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ligands.[6] An advantage of the palladium-catalysed B-addition reaction leading to the creation of a C–B bond is that it is possible to use the organoboronate intermediate to conduct a subsequent palladium-mediated reaction, for example, a cross-coupling reaction[7] or borylative cyclisation of enynes and enediynes.[8]

The tandem diboration/arylation of alkenes was first performed asymmetrically by Morken et al.[9] A Rh^{I} complex was employed for the catalytic diboration and a Pd complex served favourably for the subsequent monoarylation of the intermediate alkylboronic ester. In order to highlight the benefit of using a single complex for both transformations, we developed multifaceted palladium(II) and palladium(III) complexes[10] that participated in both catalytic cycles (diboration and arylation) with equal success.[11]

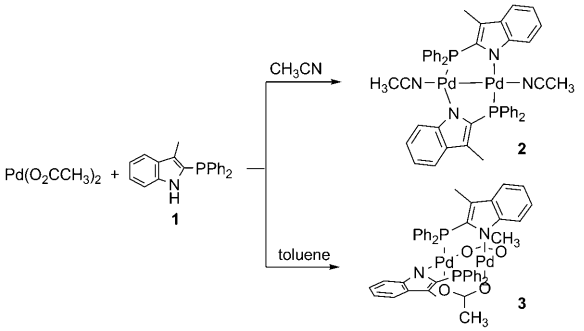
The diphenyl(3-methyl-2-indolyl)phosphine ligand synthesised by Browning et al.[12] contains an electron-rich heterocyclic indole substituent. Deprotonation of the indolyl nitrogen atom with a base gives rise to a second coordination centre, yielding a bidentate ligand with two donor centres of different Lewis basicity. This ligand may bridge two transition metal centres through the P and N atoms to afford dinuclear complexes favoured by the geometry and rigidity of the ligand. There have been a few examples in the literature of complexes with this phosphine, including dinuclear palladium and trinuclear ruthenium compounds, in which the coordination exclusively involves the phosphorus atom,[12,13] and $[Ru_3(CO)_9(\mu\text{-}H)\{\mu^3,\eta^2\text{-}P(C_6H_5)_2(C_9H_7N)\}]$, in which the ligand behaves as a novel and robust six-electron P,N-donor.[13]

We present herein the synthesis and characterisation, as well as electrochemical and catalytic studies, of new dinuclear palladium(II) complexes containing diphenyl(3-methyl-2-indolyl)phosphine as a P,N-bridging coordination ligand. The feasibility of a new β-boration/arylation tandem approach has been demonstrated for all of these complexes.

Results and Discussion

Palladium catalysts: Palladium acetate, $[Pd(O_2CCH_3)_2]$, reacts smoothly under anaerobic conditions with diphenyl(3-methyl-2-indolyl)phosphine ($C_9H_8NPPh_2$, **1**) to give dinuclear complexes with a P,N-bridging coordination mode. The composition of the complex formed depends considerably on the solvent used as the reaction medium. When $[Pd(O_2CCH_3)_2]$ was suspended in acetonitrile and $C_9H_8NPPh_2$ was added, the dinuclear palladium(I) compound $[Pd(\mu\text{-}C_9H_7NPPh_2)(NCCH_3)]_2$ (**2**) was obtained in low yield (31%). However, if the reaction was run in toluene, exclusively the palladium(II) compound $[Pd(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCH_3)]_2$ (**3**) was obtained (yield 84%) (Scheme 2). In the synthesis of **2**, a small amount of complex **3** was obtained, along with decomposition products.

Both complexes were spectroscopically and structurally characterised (Figures 1 and 2). Selected bond lengths and angles are displayed in Table 1.



Scheme 2. Synthesis of $[Pd(\mu\text{-}C_9H_7NPPh_2)(NCCH_3)]_2$ and $[Pd(\mu\text{-}C_9H_7NPPh_2)_2(\mu\text{-}O_2CCH_3)]_2$.

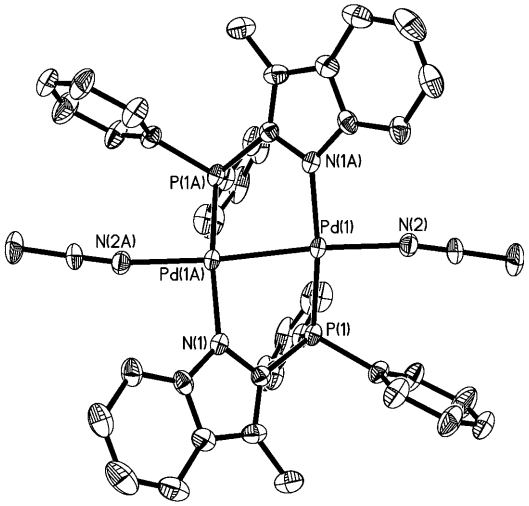


Figure 1. ORTEP view of compound **2** with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

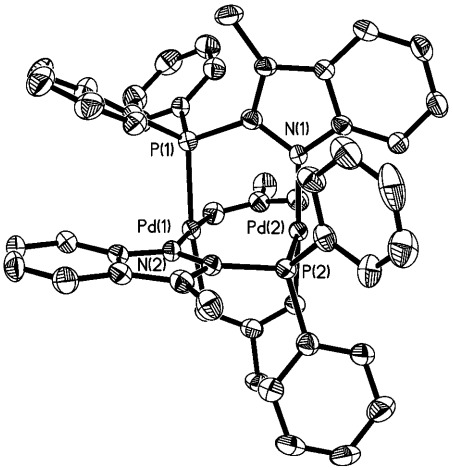


Figure 2. ORTEP view of compound **3** with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Compound **2** crystallised in the monoclinic space group *P*2/*c*. Its structure is similar to those side-by-side palladium(I) compounds with metal–metal bonds of the type

Table 1. Selected bond lengths [Å] and angles [°] for different palladium(I) and palladium(II) compounds.

Compound	**2**[a]	**3**	**4**	**7**
Pd(1)–Pd(2)	2.5459(8)	2.6884(8)	2.7521(4)	2.7395(2)
Pd(1)–P(1)	2.2275(18)	2.240(2)	2.3619(11)	2.3538(11)
Pd(2)–P(2)	–	2.240(2)	2.3619(11)	2.3538(11)
Pd(1)–P(3)	–	–	2.3435(11)	2.3268(13)
Pd(1)–N(2)	2.080(5)	1.996(6)	1.994(4)	–
Pd(2)–N(1)	2.164(6)	1.973(6)	2.034(4)	2.091(4)
Pd(2)–N(3)	–	–	2.021(4)	–
Pd(2)–N axial	2.164	–	–	–
Pd(1)–C(42)	–	–	–	2.004(5)
Pd(2)–C(72)	–	–	–	2.016(5)
P(1)-Pd(1)-Pd(2)	81.74(5)	90.14(6)	89.93(3)	91.03(3)
Pd(2)-Pd(1)-N(2)	91.15(14)	90.14(6)	90.45(10)	86.95(3)
P(1)-Pd(1)-P(3)	–	–	176.07(4)	176.36(4)

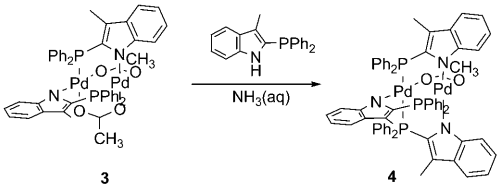
[a] Pd(2) = Pd(1A); P(2) = P(1A); N(2) = N(1A).

$[Pd_2X_2(dppm)_2]$ (X = Cl, Br, C_6Cl_5, CF_3CO_2; dppm = bis(diphenylphosphino)methane), with anionic ligands in axial positions,[14] and the cationic $[Pd_2(dppm)_2(CNtBu)_2](BF_4)_2$.[15] The two palladium atoms are bridged by two phosphine ligands in the P,N coordination mode and show an approximately square coordination with Pd–Pd interaction. Two molecules of acetonitrile in the axial positions complete the coordination. The steric and orbital interactions are minimised by a twisting about the Pd–Pd axis. The average dihedral angle (Φ) between the two coordination least-square planes formed by the two metal centres (PMMN) is 37.05°. Compounds with the $[Pd_2(dppm)_2]^{2+}$ skeleton have Φ values between 33 and 50.5°.[14,15] The Pd–Pd distance is 2.5459(8) Å, which is smaller than the corresponding distance in $[Pd_2X_2(dppm)_2]$ compounds (2.594–2.699 Å) and may indicate that acetonitrile has a weaker *trans* effect.[14] The Pd–Pd distance in $[Pd_2(dppm)_2(CNtBu)_2](BF_4)_2$ is 2.6186(12) Å.[15]

Compound **3** crystallises in the monoclinic space group $P2_1/n$. Each palladium atom is coordinated by one nitrogen atom and one phosphorus atom, each from a different $C_9H_7NPPh_2^-$ ligand, and two different carboxylate anions complete the square-planar coordination. The Pd–Pd distance of 2.6884(8) Å indicates the absence of a Pd–Pd interaction.

Compound **4** was obtained when **3** was treated with the ammonium salt of **1**, which was prepared by deprotonation at the indolyl nitrogen of **1** by adding some drops of 1 M aqueous NH_3 to a solution of this phosphine in CH_2Cl_2 (Scheme 3). Only one carboxylate anion was substituted by a P,N-bridging coordination ligand. A second ligand could not be introduced, even in the presence of an excess of the ammonium salt of **1**. Compound **4** was obtained in low yield (17%) together with an insoluble compound that was not characterised.

Compound **4** was structurally characterised by X-ray diffraction techniques (Figure 3). It crystallises in the monoclinic space group $P2(1)$. Selected bond lengths and angles are displayed in Table 1.



Scheme 3. Synthesis of $[Pd_2(\mu\text{-}C_9H_7NPPh_2)_3(\mu\text{-}O_2CCH_3)]$.

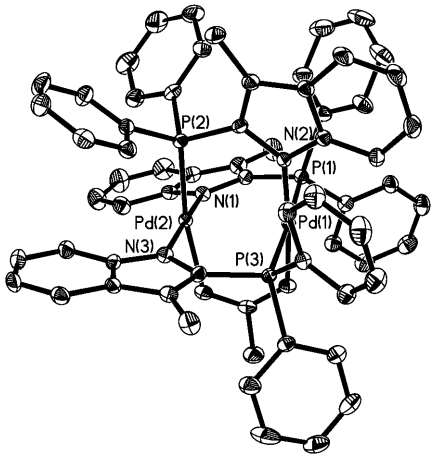
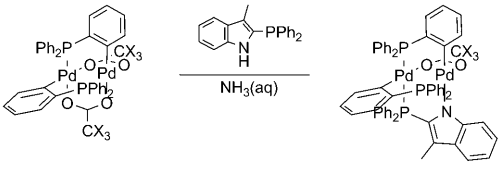


Figure 3. ORTEP view of compound **4** with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The bimetallic unit is bonded by three $C_9H_7NPPh_2^-$ ligands and one carboxylate group. The palladium atoms have different coordination environments in a square-planar coordination mode. The substitution of one carboxylate group by a $C_9H_7NPPh_2^-$ group increases the Pd–Pd distance in **4** (2.752(4) Å vs. 2.6884(8) Å in **3**). Again, there is no Pd–Pd interaction. The Pd(2)–P(2) (P *trans* to O) distance of 2.2525(1) Å is smaller than the Pd(1)–P(1) (2.3619(11) Å) and Pd(1)–P(3) (2.3435(11) Å) distances when P is *trans* to P. The Pd(1)–N(2) distance with N *trans* to O is also smaller than the Pd(2)–N(1) and Pd(2)–N(3) distances (N *trans* to N) (see Table 1).

The same behaviour was observed when the *ortho*-metalated compounds $[Pd_2(C_6H_4PPh_2)_2(\mu\text{-}O_2CCX_3)_2]$ (X = H (**5**); X = F (**6**)) were reacted with the ammonium salt of **1** (Scheme 4). Again, only one $C_9H_7NPPh_2^-$ ligand was coordinated. Compounds **7** and **8** were obtained in high yields (85



Scheme 4. Synthesis of $[Pd_2(\mu\text{-}C_6H_4PPh_2)_2(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCX_3)]$ (X = H (**7**); X = F (**8**)).

and 80%, respectively). Both complexes were characterised spectroscopically and **7** was also characterised by X-ray diffraction analysis (Figure 4).

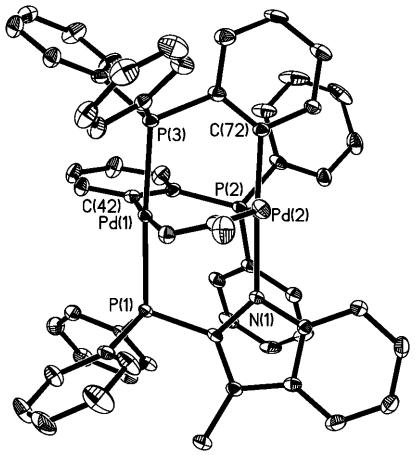


Figure 4. ORTEP view of compound **7** with ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Compound **7** crystallises in the triclinic space group $P\bar{1}$. Selected bond lengths and angles are displayed in Table 1. In this case, the two palladium atoms are bridged by two *ortho*-metalated triphenylphosphine ligands, one $C_9H_7NPPh_2^-$ ligand, and one carboxylate group. The Pd(1)–Pd(2) distance of 2.7395(5) Å is similar to that observed in compound **4**. The Pd(2)–P(2) (P *trans* to O) distance is smaller than the Pd(1)–P(1) and Pd(1)–Pd(3) distances (see Table 1).

Electrochemical study: Cyclic voltammetry showed that the dinuclear palladium(II) compounds **3**, **4**, **7**, and **8** had one A/C couple in their initial anodic scans between 1 and 1.5 V. Figure 5 shows the cyclic voltammogram of **4** in 0.10 M Bu_4NPF_6 in CH_2Cl_2 (for the voltammograms of **3**, **7**, and **8**, see Figures S1, S2, and S3 in the Supporting Information). Table 2 displays the potential values in volts of the anodic and cathodic peaks and the A/C couples (half of the sum of the anodic and cathodic peaks) versus AgCl/Ag. The A/C couple can be described in terms of a reversible or pseudo-reversible single-electron transfer. The observed electrochemical behaviour can be described as a one-electron transfer process. No second A/C couple was observed at the potential values studied.

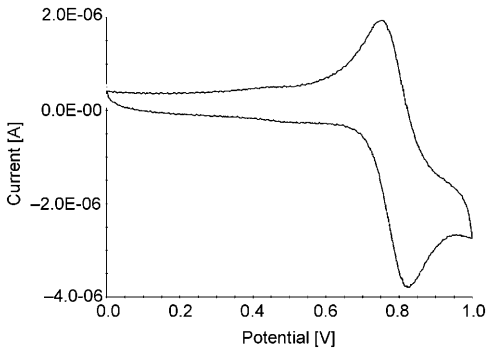


Figure 5. Cyclic voltammogram of compound **4** in CH_2Cl_2.

Table 2. Potential values of the anodic and cathodic peaks and the A/C couples.

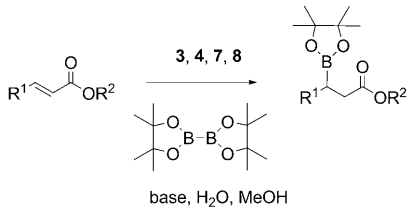
Compound	Anodic peak potential, A [V]	Cathodic peak potential, C [V]	A/C couple [V]
3	1.042	0.882	0.962
4	0.838	0.759	0.798
7	0.637	0.547	0.592
8	0.714	0.585	0.650

These values were compared with those obtained for compounds **5** and **6** under the same conditions. In a previous paper, we described how A/C couple potential values decrease with increasing electron-donating ability of the carboxylate group in compounds with two carboxylate bridging ligands.[10c] The substitution of one carboxylate anion in **5** and **6** by one P,N-bridging coordination ligand considerably decreased the A/C couple electrode potentials in compounds **7** (0.592 vs. 0.898 V in **5**) and **8** (0.650 vs. 0.678 V in **6**). The same behaviour was observed when we compared the electrochemical properties of **3** and **4**. Again, the compound with one carboxylate group, **4**, showed a lower A/C couple electrode potential (0.798 vs. 0.962 V). By comparing the A/C couple potential data in Table 2, we were able to propose the following order for the electron-donating abilities of the ligands in compounds **3**–**8**: $[\mu\text{-}C_6H_4PPh_2]^- > [\mu\text{-}C_9H_7NPPh_2]^- > CH_3CO_2^- > CF_3CO_2^-$.

Palladium(III) compounds: In spite of the reversible or pseudo-reversible electrochemical behaviour observed for **3**, **4**, **7**, and **8**, the oxidation reaction with $PhI{\cdot}Cl_2$ did not stabilise palladium(III) complexes and different results were obtained. Whereas no reaction was observed with **3** and **4**, compounds **7** and **8** gave unstable palladium(III) complexes.

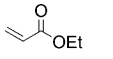
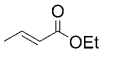
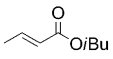
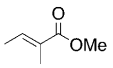
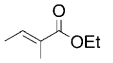
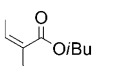
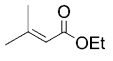
The reactions of **4** and **8** with $PhI{\cdot}Cl_2$ were monitored by ^{31}P NMR spectrometry between −60 and 25 °C and between −60 and 35 °C, respectively. No changes in the spectrum of **4** at different temperatures were observed after the addition of $PhI{\cdot}Cl_2$, indicating that no reaction took place. The spectrum of **8**, on the other hand, recorded at −60 °C immediately after the addition of $PhI{\cdot}Cl_2$, showed two singlet signals at $\delta = 28$ and -10 ppm (1:2.5 ratio). The signal at $\delta = 28$ ppm did not disappear when the temperature was increased and was attributed to the stable tetranuclear compound $[Pd(C_6H_4PPh_2)Cl]_4$.[4b] We observed that the dinuclear palladium(III) compounds $[Pd_2(C_6H_4PPh_2)_2(\mu\text{-}O_2CCX_3)_2Cl_2]$ evolve in solution at room temperature to this stable tetranuclear product.[11] The minor signal at $\delta = -10$ ppm was no longer seen in the spectrum recorded at 0 °C, and most likely corresponded to an unstable palladium(III) compound[10d,11] that did not contain diphenyl(3-methyl-2-indolyl)phosphine as a P,N-bridging coordination ligand, probably a palladium(III) derivative of $[Pd(C_6H_4PPh_2)Cl]_4$.

Catalytic β-boration of α,β-unsaturated carbonyl compounds: In the course of studying the palladium-catalysed β-boration of α,β-unsaturated carbonyl compounds, we selected α,β-unsaturated esters, ketones, aldehydes, and amides as suitable substrates. The catalytic influence was first established when 2.5 mol% loadings of the dinuclear palladium complexes **3**, **4**, **7**, and **8** were used as catalytic precursors in the reactions of ethyl acrylate or (*E*)-ethyl but-2-enoate with bis(pinacolato)diboron (B_2pin_2) in toluene (Scheme 5). In all cases, the β-boration was complete within 6 h at room temperature (Table 3, entries 1–8). The presence of a base and MeOH appeared to be crucial for high conversions[2a]



Scheme 5. Pd-mediated β-boration of α,β-unsaturated esters.

Table 3. Catalytic β-boration of α,β-unsaturated esters with B_2pin_2 mediated by palladium complexes.[a]

Entry	Substrate	Catalytic system	*t* [h]	Conv. [%][b]
1		**3**	6	99
2		**4**	6	99
3		**7**	6	99
4		**8**	6	99
5		**3**	6	99
6		**4**	6	99
7		**7**	6	99
8		**8**	6	99
9		**3**	6	99
10		**4**	6	64
11		**7**	6	47
12		**7**	24	57
13		**8**	6	81
14		**3**	6	94
15		**3**	16	50
16		**4**	16	51
17		**7**	16	51
18		**8**	16	33
19		**3**	24	27
20		**3**	6	99
21		**8**	6	62

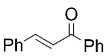
[a] Standard conditions: substrate/Pd 1:0.05; B_2pin_2 (1.5 equiv), Cs_2CO_3 (1.5 equiv), H_2O (1.5 equiv), MeOH (1 equiv); solvent: toluene (2 mL); $T=25$ °C. [b] Determined by ^1H NMR spectrometry.

and THF could be used as the solvent with equal efficiency. On the basis of the results obtained with these model substrates, and with the aim of exploring the scope of these Pd catalytic systems, we performed a series of experiments with a range of substrates under the optimised conditions.

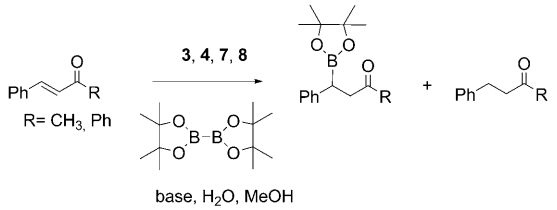
The substrate (*E*)-isobutyl but-2-enoate, with a bulkier ester moiety, was also efficiently β-borated with catalytic system **3**, but less so with **4**, **7**, and **8** (Table 3, entries 9–13), even after longer reaction times. A similar trend was observed when α-substituted α,β-unsaturated esters were used in the reaction, in that while (*E*)-methyl 2-methylbut-2-enoate was conveniently transformed into the β-organoborated product with catalytic system **3** (Table 3, entry 14), the analogous substrates (*E*)-ethyl 2-methylbut-2-enoate and (*Z*)-isobutyl 2-methylbut-2-enoate were only β-borated with low or moderate conversions, even after reaction times of 16 or 24 h (Table 3, entries 15–19). Therefore, the nature of the ester moiety seems to play an important role in the β-boration reaction as far as the substrate is concerned, and catalytic system **3** seems to be the most efficient, probably because it contains only two P,N ligands. This behaviour could also be observed when complexes **3** and **8** were used to mediate the β-boration of β-substituted ethyl 3-methylbut-2-enoate, since complex **3** favoured complete conversion while complex **8** only transformed 62% of the substrate into the desired product (Table 3, entries 20 and 21).

We next explored the β-boration of related α,β-unsaturated ketones, which has only been explored previously in the literature with Cu^I complexes as catalytic systems.[2c,16] Catalytic complexes **3**, **4**, **7**, and **8** were found to mediate the β-boration of methyl vinyl ketone, both in toluene and THF (Table 4, entries 1–4). However, when (*E*)-4-phenylbut-3-en-2-one was used as substrate, the conversion and selectivity diminished significantly, depending on the catalytic system (Table 4, entries 5–10). It was observed that β-phenyl-substituted vinyl ketones favoured the formation of a non-borylated saturated byproduct (Scheme 6).

Table 4. Catalytic β-boration of α,β-unsaturated ketones with B_2pin_2 mediated by palladium complexes.[a]

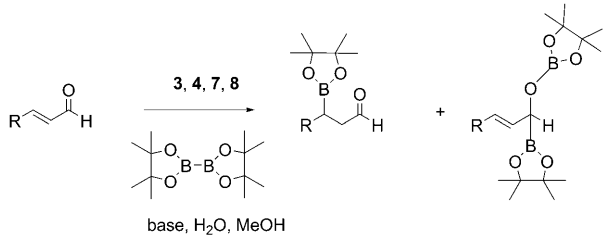
Entry	Substrate	Catalytic system	Conv. [%][b]	Chem. [%][c]
1		3	99	100
2		4	99	100
3		7	99	100
4		8	99	100
5		3	85	65
6		4	31	77
7		7	80	76
8		3	93	64
9		4	22	66
10		8	93	71

[a] Standard conditions: substrate/Pd = 1:0.05; B_2pin_2 (1.5 equiv), Cs_2CO_3 (1.5 equiv), H_2O (1.5 equiv), MeOH (1 equiv); solvent: toluene (2 mL); $T=25$ °C; $t=6$ h. [b] Determined by ^1H NMR spectrometry. [c] Chemoselectivity in favour of the β-borated product, determined by ^1H NMR spectrometry.



Scheme 6. Pd-mediated β-boration of α,β-unsaturated ketones.

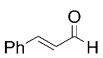
Metal-catalysed β-boration of the most challenging α,β-unsaturated aldehydes has hitherto only been reported in two cases using Rh[17] and Pt[18] catalysts and by our group using Cu complexes.[2d,e] Its difficulty stems from the fact that there tends to be competing 1,2-diboron addition (Scheme 7). Considering the benefits of palladium-mediated



Scheme 7. Pd-mediated β-boration of α,β-unsaturated aldehydes.

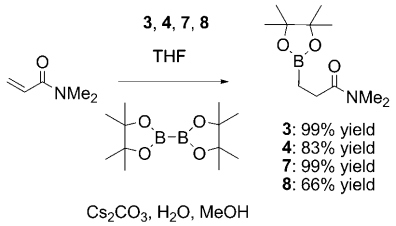
B-addition reactions,[4] we decided to examine the use of **3**, **4**, **7**, and **8** as catalysts for the β-boration of acrolein as a model substrate. As can be seen in Table 5, the transformation of the substrate into the desired organoborated product was, depending on the catalytic system, achieved with moderate to high levels of conversion (entries 1–3). Complex **3** was seen to be similarly effective in catalysing the β-boration of crotonaldehyde (Table 5, entries 4 and 5). However, the β-boration of cinnamaldehyde was less chemoselective when MeOH and H_2O were added (Table 5, entries 6 and 7).

Table 5. Catalytic β-boration of α,β-unsaturated aldehydes with B_2pin_2 mediated by palladium complexes.[a]

Entry	Subst.	Cat. system	Additives	Conv. [%][b]	Sel. [%][c]
1		3	$MeOH/H_2O$	94	98
2		4	$MeOH/H_2O$	82	74
3		8	$MeOH/H_2O$	97	87
4		3	$MeOH/H_2O$	97	83
5		3	–	96	92
6		3	$MeOH/H_2O$	75	23
7		3	–	51	100

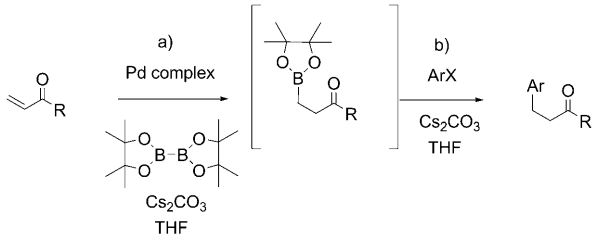
[a] Standard conditions: substrate/Pd = 1:0.05; B_2pin_2 (1.5 equiv), Cs_2CO_3 (1.5 equiv), H_2O (1.5 equiv), MeOH (1 equiv); solvent: toluene (2 mL); $T = 25\,°C$; $t = 6$ h. [b] Determined by ^1H NMR spectrometry. [c] Selectivity in favour of the β-borated product, determined by ^1H NMR spectrometry.

The metal-catalysed β-boration of α,β-unsaturated amides was first performed by Oshima[19] using Ni^{II} complexes. It was revealed that amides reacted with B_2pin_2 much more rapidly than the corresponding esters. Similarly, Molander et al.[16] reported the preparation of trifluoroboratohomoenolates from tertiary α,β-unsaturated amides by employing Cu^I salts and KHF_2. The asymmetric version was conducted by Yun et al.[20] using Cu^I catalytic systems modified with chiral bidentate ligands. In this context, this study has shown for the first time that palladium complexes can efficiently perform conjugate boration on α,β-unsaturated amides. As can be seen in Scheme 8, the tertiary amide dimethyl acrylamide was quantitatively converted into the corresponding β-borated product within a reasonable reaction time (6 h), in both toluene and THF.



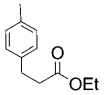
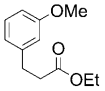
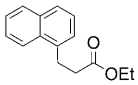
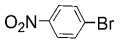
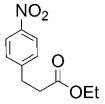
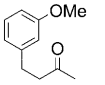
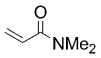
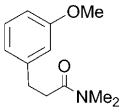
Scheme 8. Pd-mediated β-boration of α,β-unsaturated amides.

Catalytic Suzuki reaction: Finally, we checked whether palladium-based complexes could be used to catalyse single-pot diboration/Suzuki–Miyaura cross-coupling when only 2.5 mol% of a given palladium dinuclear complex was present throughout the tandem reaction (Scheme 9). We were very pleased to observe that complex **7** catalysed both the β-boration of ethyl acrylate or methyl vinyl ketone and the subsequent cross-coupling with a range of aryl bromides, although conversions were only moderate after 24 h of reaction (Table 6, entries 1–5). However, the β-boration of dimethyl acrylamide with B_2pin_2 was efficiently completed after the addition of 3-bromoanisole with two equivalents of Cs_2CO_3 and H_2O. The β-arylation proceeded to completion (Table 6, entry 6). THF was the solvent of choice for the two consecutive reactions, because the use of toluene reduced the efficiency of the cross-coupling transformation.



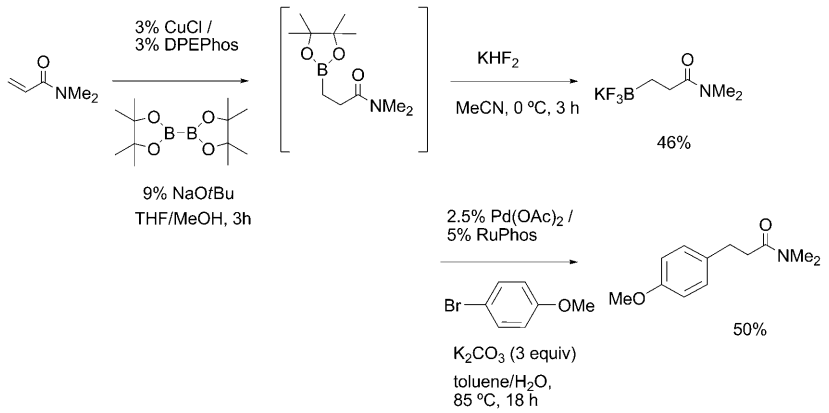
Scheme 9. Pd-mediated tandem single-pot diboration/Suzuki–Miyaura cross-coupling. a) β-boration, b) arylation.

Table 6. Catalytic tandem sequence of β-boration/arylation of α,β-unsaturated carbonyl compounds mediated by palladium complex **7**.[a]

Entry	Subst.	ArX	Prod.	Conv. [%][b]
1				31
2				28
3				14
4				55
5				46
6				99 (89[c])

[a] Standard conditions for β-boration: substrate/Pd = 1:0.05; B_2pin_2 (1.5 equiv), Cs_2CO_3 (1.5 equiv), H_2O (1.5 equiv), MeOH (1 equiv); solvent: THF (2 mL); $T = 25\,°C$; $t = 6$ h. Standard conditions for cross-coupling: ArX (2 equiv) and Cs_2CO_3 (3 equiv), reflux for 24 h. [b] Determined by ^1H NMR spectrometry. [c] Isolated yield.

The amide homoenolate cross-coupling reaction has only been reported by Molander et al.,[16] and their yields were moderate even when the potassium trifluoroboratohomoenolate analogue was used. While they required two different catalytic systems (Cu^I/DPEPhos/NaO*t*Bu and Pd^{II}/RuPhos/K_2CO_3; DPEPhos = bis(2-diphenylphosphinophenyl) ether, RuPhos = (3-diethoxyphosphinothioylsulfanyl-1,4-dioxan-2-yl)sulfanyldiethoxysulfanylidenephosphorane) to perform the three steps (Scheme 10), we only needed the dinuclear palladium complex as a single catalytic system in a one-pot protocol. Similar behaviour has been found for related Pd_2^{6+} and Pd_2^{4+} complexes as synthetic precursors for mediating the tandem diboration–arylation reactions of alkenes by using a single catalyst. These examples show for the first time the multifaceted properties of a palladium complex in participating in different catalytic cycles through organoborane intermediates with equal efficacy.



Scheme 10.

Conclusion

Stable dinuclear complexes with P,N-bridging coordination have been synthesised in high yield. They showed high activity and selectivity in the catalytic β-boration of α,β-unsaturated esters, ketones, aldehydes, and amides. More remarkably, an "in situ" catalytic tandem reaction has been designed, in which the C_β–B bond is transformed into a targeted C_β–Ar bond. Advantageously, the same catalyst promotes both steps, with moderate to high conversion of the substrate. In spite of the reversible or pseudo-reversible electrochemical behaviour observed for all of the compounds, no stabilised palladium(III) complexes have been obtained.

Experimental Section

General: Commercially available $[Pd(O_2CCH_3)_2]$ was purchased from Pressure Chemical. All solvents were of analytical grade. $C_9H_8NPPh_2$ (**1**),[12] PhI·Cl_2,[21] and $[Pd(C_6H_4PPh_2)(\mu\text{-}O_2CCX_3)]_2$ (X = H (**5**); F (**6**))[10a–c] were synthesised according to the methods described in the literature. Column chromatography was performed on silica gel (35–70 mesh). Solvent mixtures are volume/volume mixtures, unless otherwise specified. All reactions were carried out in oven-dried glassware under argon atmosphere using Schlenk techniques, although the isolated solids are air-stable. ^1H and $^{13}C\{^1H\}$ NMR (using the residual proton signal of $CDCl_3$ as reference) and $^{19}F\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR (with standard references) spectra were recorded on a Bruker Avance 400 MHz spectrometer from samples in $CDCl_3$ solutions at 25 °C, unless otherwise specified. Chemical shifts are reported in ppm. Coupling constants (*J*) are given in hertz (Hz). Elemental analyses were provided by the Centro de Microanalisis Elemental, Universidad Complutense de Madrid.

Synthesis of $[Pd(\mu\text{-}C_9H_7NPPh_2)(NCCH_3)]_2$ (2): $[Pd(O_2CCH_3)_2]$ (100 mg, 0.446 mmol) was first suspended in acetonitrile (6 mL). The suspension was degassed (two freeze–pump–thaw cycles), $C_9H_8NPPh_2$ (140 mg, 0.444 mmol) was added in a flow of argon, and the mixture was degassed again. Upon reaching room temperature, the reaction mixture darkened and an orange precipitate formed within minutes. The mixture was then stirred overnight in the absence of light. Thereafter, the precipitate was collected by filtration, washed with acetonitrile (2 × 3 mL), and vacuum dried. The crude complex was extracted with a CH_2Cl_2/CH_3CN mixture (5:1). The dark-red solution was twice passed through a column filled with cotton wool (1.5 × 10 cm). The resulting orange solution was layered with CH_3CN and set aside for evaporation of the volatiles at room temperature in the absence of light. Bright orange-red crystals were obtained, which were

washed with acetonitrile and vacuum-dried (64 mg, 31%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of the solvents from a solution of **2** in CH_2Cl_2/CH_3CN at room temperature. ^{1}H NMR (CD_2Cl_2 + two drops of [D_3]acetonitrile): $\delta = 1.76$ (s, 6H; CH_3), 1.96 (s, unspecified amount, acetonitrile), 6.81 (t, $^1J = 7.8$ Hz, 2H), 6.91 (t, $^1J = 8.0$ Hz, 2H), 7.28 (m, 8H), 7.42 ppm (m, 16H); ^{31}P{^{1}H} (CD_2Cl_2 + two drops of [D_3]acetonitrile): $\delta = -2.5$ ppm (s); elemental analysis calcd (%) for $C_{46}H_{40}N_4P_2Pd_2$: C 59.82, H 4.37, N 6.07; found: C 59.37, H 4.38, N 6.02.

X-ray crystal structure data for compound 2: $C_{46}H_{40}N_4P_2Pd_2\cdot 3H_2O$, monoclinic, space group $P2/c$, $a = 13.8460(4)$, $b = 8.8460(3)$, $c = 18.8590(6)$ Å, $\beta = 91.352(2)°$, $V = 2309.24(13)$ Å^3, $Z = 2$, crystal dimensions: $0.24 \times 0.22 \times 0.20$ mm; $Mo_{K\alpha}$ radiation, 273(2) K; 8754 reflections, 5022 independent; $\mu = 0.889$ mm^{-1}; refinement (on F^2) with SHELXTL (version 6.1), 259 parameters, 0 restraints, $R_1 = 0.0659$ ($I > 2\sigma$) and wR_2 (all data) = 0.2112, GOF = 1.065, max/min residual electron density: 1.291/−1.386 e Å^{-3}.

CCDC 771070 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Pd(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCH_3)]_2$ (3): $[Pd(O_2CCH_3)_2]$ (80 mg, 0.357 mmol) was suspended in toluene (10 mL), the suspension was degassed (three freeze–pump–thaw cycles), and then $C_9H_8NPPh_2$ (112 mg, 0.356 mmol) was added in a flow of argon. The reaction mixture darkened immediately and the deep-red solution obtained was stirred for 10 h. The solvent was then removed under vacuum and the crude product was extracted with diethyl ether (4 × 5 mL). The solvent was evaporated from the combined extracts, and the brownish-red solid was briefly washed with hexanes (2 × 3 mL) and recrystallised from a hexane/diethyl ether mixture (145 mg, 84%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation of the solvent from a solution of **3** in hexane at room temperature. ^{1}H NMR: $\delta = 1.08$ (s, 6H; bridging acetate), 1.65 (s, 6H; methyl), 6.53 (br s, 4H), 6.65 (br s, 4H), 6.75 (m, 4H), 7.03 (t, $J = 7.2$ Hz, 2H), 7.35 (dd, $J = 6.8$ Hz, $J = 4.2$ Hz, 2H), 7.45 (m, 2H), 7.50 (m, 6H), 7.72 ppm (m, 4H); ^{13}C{^{1}H} NMR: $\delta = 11.4$ (s), 22.7 (s), 115.9 (s), 117.3 (s), 118.6 (s), 122.3 (s), 123.9, 124.7, 126.6, 127.2, 127.9, 128.4, 129.9, 130.7, 131.1, 131.5, 134.1, 145.3, 183.0 ppm; ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): $\delta = 4.1$ ppm (s); elemental analysis calcd (%) for $C_{46}H_{40}N_2O_4P_2Pd_2$: C 57.57, H 4.20, N 2.92; found: C 57.42, H 4.30, N 2.94.

X-ray crystal structure data for compound 3: $C_{46}H_{40}N_2O_4P_2Pd_2\cdot C_4H_{10}O$, monoclinic, space group $P2_1/n$, $a = 11.5900(2)$, $b = 20.3330(4)$, $c = 20.5630(5)$ Å, $\beta = 92.7330(7)°$, $V = 92.7330$ Å^3, $Z = 4$, crystal dimensions: $0.27 \times 0.22 \times 0.19$ mm; $Mo_{K\alpha}$ radiation, 273(2) K; 8248 reflections, 8248 independent; $\mu = 0.855$ mm^{-1}; refinement (on F^2) with SHELXTL (version 6.1), 555 parameters, 0 restraints, $R_1 = 0.0750$ ($I > 2\sigma$) and wR_2 (all data) = 0.2141, GOF = 1.098, max/min residual electron density: 1.478/−1.485 e Å^{-3}.

CCDC 771071 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Pd_2(\mu\text{-}C_9H_7NPPh_2)_3(\mu\text{-}O_2CCH_3)]$ (4): $[Pd(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCH_3)]_2$ (**3**) (50 mg, 0.052 mmol) was dissolved in CH_2Cl_2 (15 mL) under an argon atmosphere and then a solution of $C_9H_8NPPh_2$ (20 mg, 0.063 mmol) in CH_2Cl_2 (8 mL) containing two drops of 20% aqueous NH_3 was added. The reaction mixture was stirred overnight and then dried with Na_2SO_4. The solvent was removed under vacuum. The residual oil was dissolved in CH_2Cl_2/hexane (1:1; 5 mL) and chromatographed on a column of silica (2 × 30 cm). Elution with CH_2Cl_2/hexane (1:1) led to the separation of a red band, from which a red solid was crystallised (11 mg, yield 17%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of **4** in CH_2Cl_2 at room temperature. ^{1}H NMR: $\delta = 0.63$ (s, 3H), 1.40 (s, 3H), 1.56 (s, 6H), 6.56 (m, 5H), 6.64–6.74 (m, 16H), 6.87–6.92 (m, 5H), 6.99 (t, $J = 7$ Hz, 2H), 7.15–7.19 (m, 4H), 7.55–7.33 (m, 6H), 8.44 ppm (d, $J = 8$ Hz, 2H); ^{13}C{^{1}H} NMR: $\delta = 11.4$ (s), 12.0 (s), 23.2 (d, $J = 4$ Hz), 115–146 (C_{arom}), 182.0 ppm (d, $J = 3$ Hz); ^{31}P{^{1}H} NMR: $\delta = -0.9$ (d, $J = 11$ Hz), 1.3 ppm (t, $J = 11$ Hz); elemental analysis calcd (%) for $C_{65}H_{54}N_3O_2P_3Pd_2$: C 64.26, H 4.45, N 3.46; found: C 64.72, H 4.75, N 3.33.

X-ray crystal structure data for compound 4: $C_{65}H_{54}Cl_4N_3O_2P_3Pd_2\cdot 2CH_2Cl_2$, monoclinic, space group $P2(1)$, $a = 15.1620(3)$, $b = 11.4900(2)$, $c = 17.4600(3)$ Å, $\beta = 92.5110(9)°$, $V = 3038.81(10)$ Å^3, $Z = 2$, crystal dimensions: $0.25 \times 0.23 \times 0.20$ mm; $Mo_{K\alpha}$ radiation, 273(2) K; 13059 reflections, 13059 independent; $\mu = 0.895$ mm^{-1}; refinement (on F^2) with SHELXTL (version 6.1), 730 parameters, 1 restraint, $R_1 = 0.0402$ ($I > 2\sigma$) and wR_2 (all data) = 0.1166, GOF = 1.128, max/min residual electron density: 0.691/−1.172 e Å^{-3}.

CCDC 771072 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Pd_2(\mu\text{-}C_6H_4PPh_2)_2(\mu\text{-}C_9H_7NPPh_2)(\mu\text{-}O_2CCX_3)]$ (X = H (7); X = F (8)): $[Pd_2(C_6H_4PPh_2)_2(\mu\text{-}O_2CCX_3)_2]$ (X = H (**5**); X = F (**6**)) (0.117 mmol) was dissolved in CH_2Cl_2 (15 mL) and a stoichiometric amount of $C_9H_8NPPh_2$ (40 mg, 0.117 mmol) in CH_2Cl_2 (3 mL) containing two drops of 20% aqueous NH_3 was added. The yellow reaction mixture was stirred for 2 h, dried with Na_2SO_4, and filtered through siliceous earth. Complexes **7** and **8** were obtained as yellow crystalline solids (**7**: 85%, **8**: 80%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of **7** in CH_2Cl_2 at −20 °C.

Compound 7: ^{1}H NMR: $\delta = 0.75$ (s, 3H), 1.54 (s, 3H), 6.53 (m, 2H), 6.61–6.75 (m, 6H), 6.80–7.00 (m, 8H), 7.05–7.15 (m, 6H), 7.18–7.22 (m, 4H), 7.30–7.38 (m, 6H), 7.40–7.50 (m, 10H), 8.45 ppm (d, $J = 8.2$ Hz, 2H); ^{13}C{^{1}H} NMR: $\delta = 12.0$ (s), 12.0 (s), 24.2 (s), 115–146 (C_{arom}), 163.4 (s), 168 (s), 180 ppm (s); ^{31}P{^{1}H} NMR: $\delta = 2.6$ (dd, $J = 365$ Hz, $J = 22$ Hz), 13.8 (dd, $J = 365$ Hz, $J = 28$ Hz), 18.3 ppm (dd, $J = 28$ Hz, $J = 22$ Hz); elemental analysis calcd (%) for $C_{62}H_{51}N_2O_2P_3Pd_2$: C 64.10, H 4.39, N 2.41; found: C 63.41, H 4.73, N 3.15.

X-ray crystal structure data for compound 7: Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of **7** in CH_2Cl_2 at −20 °C. $C_{59}H_{47}Cl_3NO_2P_3Pd_2\cdot(0.5\,C_6H_{14},\ CHCl_3)$, triclinic, space group P-1, $a = 12.9230(3)$, $b = 14.2270(3)$, $c = 18.3890(3)$ Å, $\alpha = 94.5370°$, $\beta = 94.6850(13)°$, $\gamma = 116.1441°$, $V = 2999.74$ Å^3, $Z = 2$, crystal dimensions: $0.26 \times 0.25 \times 0.20$ mm; $Mo_{K\alpha}$ radiation, 273(2) K; 10153 reflections, 10153 independent; $\mu = 0.855$ mm^{-1}; refinement (on F^2) with SHELXTL (version 6.1), 660 parameters, 0 restraints, $R_1 = 0.0569$ ($I > 2\sigma$) and wR_2 (all data) = 0.1900, GOF = 1.137, max/min residual electron density: 1.010/−1.851 e Å^{-3}.

CCDC 771073 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 8: ^{1}H NMR: $\delta = 1.78$ (s, 3H), 6.45 (m, 2H), 6.66 (m, 4H), 6.92 (m, 2H), 7.06 (m, 4H), 7.16 (m, 4H), 7.2 (m, 8H), 7.50 (m, 8H), 7.59 (m, 4H), 7.66 (m, 4H), 7.73 ppm (m, 2H); ^{13}C{^{1}H} NMR: $\delta = 12.0$ (s), 12.0 (s), 24.2 (s), 115–146 (C_{arom}), 163.4 (s), 168 (s), 180 ppm (s); ^{31}P{^{1}H} NMR: $\delta = 1.5$ (dd, $J = 360$ Hz, $J = 22$ Hz), 11.4 (dd, $J = 360$ Hz, $J = 32$ Hz), 19.5 ppm (dd, $J = 32$ Hz, $J = 22$ Hz); ^{19}F{^{1}H} NMR: $\delta = -77.6$ ppm (s); elemental analysis calcd (%) for $C_{62}H_{48}N_2F_3O_2P_3Pd_2$: C 61.25, H 3.95, N 2.30; found: C 60.83, H 4.05, N 2.90.

Electrochemical measurements: Cyclic voltammetry was carried out in a 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 at 25 °C, using a three-electrode configuration (platinum disk as working electrode, platinum wire as counter electrode, and an aqueous AgCl (3 M KCl) Ag electrode separated from the bulk solution by a salt bridge containing the solvent and supporting electrolyte as reference electrode) on a 273A PAR potentiostat. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as an internal reference.

Typical catalytic β-boration of α,β-unsaturated compounds: The respective palladium complex (**3**, **4**, **7**, or **8**) (0.003 mmol) was suspended in toluene or THF (2 mL) under argon in a Schlenk flask. Bis(pinacolato)diboron (47.75 mg, 0.18 mmol) was added, the suspension was stirred for

10 min, and then Cs_2CO_3 (61 mg, 0.18 mmol) was added. A solution of α,β-unsaturated ester, ketone, aldehyde, or amide (0.125 mmol) in toluene or THF (2 mL) was then added. Finally, MeOH (1.57 mmol) and water (0.18 mmol) were added and the mixture was stirred at room temperature for 6 h. The products obtained were analysed by ^{1}H NMR spectroscopy to determine their identity and the degree of conversion.

Typical catalytic diboration, subsequent Suzuki reaction, and oxidation: Bis(pinacolato)diboron (47.75 mg, 0.18 mmol) was added to a solution of the palladium dimer (2.5 mol%, 0.003 mmol Pd) and Cs_2CO_3 (61 mg, 0.18 mmol, 1.5 equiv) in THF (2 mL) under argon. The solution was stirred for 5 min, and then the α,β-unsaturated carbonyl substrate (0.12 mmol) was added followed by MeOH (63 μL, 1.57 mmol) and water (5 μL, 0.18 mmol), and stirring was continued for 6 h at room temperature. After heating to reflux, Cs_2CO_3 (122.18 mg, 0.37 mmol), the corresponding halide (0.25 mmol), and water (degassed, 0.2 mL, 10% of the solvent) were added and the reaction mixture was stirred for 24 h. After cooling, the reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic phases were washed with brine (20 mL), dried over magnesium sulfate, and dried in vacuo. The products obtained were analysed by ^{1}H NMR spectroscopy to determine their identity and the degree of conversion.

3-Methoxyphenylpropanoic acid dimethyl amide: Purification by column chromatography on silica eluting with petroleum ether/dichloromethane (3:1) → petroleum ether/ethyl acetate (1:1). ^{1}H NMR: $\delta = 2.66$ (t, 2H, $J = 7.2$ Hz; Ar-CH_2-CH_2-), 2.91 (m, 8H), 3.73 (s, 3H; OCH_3), 6.80–6.70 (m, 2H), 7.20 (t, 1H, $J = 7.6$ Hz), 7.25 ppm (s, 1H); ^{13}C{^{1}H} NMR: $\delta = 29$ (CH_2-CH_2-N$(CH_3)_2$), 35 (-N$(CH_3)_2$), 37 (-OCH_3), 55 (CH_2-CH_2-N$(CH_3)_2$), 111 (C_{arom}), 114 (C_{arom}), 120 (C_{arom}), 129 (C_{arom}), 143 (C_{arom}), 159 (C_{arom}–OMe), 172 ppm (CO); GC-MS: *m/z*: 177, 133, 120, 105, 91, 72, 58, 45.

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