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Platinum catalysed 3,4- and 1,4-diboration of α,β-unsaturated carbonyl compounds using *bis*-pinacolatodiboron

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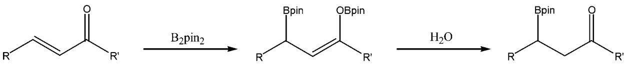
***Bis*-pinacolatodiboron reacts with α,β-unsaturated carbonyl compounds to give 1,4- and unprecedented 3,4-additions in the presence of a second generation Pt(0) catalyst at ambient temperature.**

Boronate esters and boronic acids are extremely useful in synthesis[1] and can also display biological activity.[2] It is not possible to introduce boronate groups at a position β- to a carbonyl using conventional hydroboration methods as the boron would avoid the electrophilic site.[3] In one of the earliest examples of metal catalysed hydroboration,[4] a nido-carborane anion was used as a source of B–H in the $Rh(PPh_3)_2^+$-catalysed 3,4-addition of this B–H bond to the C=C bond in butylacrylate, yielding the substituted carborane anion in which the boron is attached to $C_β$. Subsequently, Evans and Fu showed[5] that $Rh(PPh_3)_3Cl$ catalysed the conjugate 1,4-addition of catecholborane (HBcat, cat = $1,2\text{-}O_2C_6H_4$) to α,β-unsaturated amides, ketones and esters yielding useful boron enolates which, upon hydrolysis, gave the alkene reduction product. Catalysed diboration[6] of α,β-unsaturated carbonyl compounds[7–11] represents an interesting approach to the simultaneous incorporation of a boronate moiety at $C_β$ and the formation of a hydrolytically sensitive boron enolate (Scheme 1). Such reactions have recently been reported, using Pt,[7,8] Rh[9] and Cu[10,11] -based reagents.

The first reported diboration of α,β-unsaturated carbonyl compounds[7] utilised 5 mol% $Pt(PPh_3)_2(η\text{-}C_2H_4)$ as the catalyst precursor in toluene at 80 °C for 12 h with B_2pin_2 (pin = $OCMe_2CMe_2O$) and B_2cat_2. The products were characterised as the *Z*-(O) isomers of the 1,4-adducts by ^1H NMR spectroscopy. Srebnik[8] subsequently employed 5 mol% $Pt(PPh_3)_4$ as catalyst precursor at 110 °C for 20 h with B_2pin_2. Recently, Kabalka *et al.* reported[9] that 10 mol% $Rh(PPh_3)_3Cl$ catalysed the addition of B_2pin_2 and B_2neop_2 (neop = $OCH_2CMe_2CH_2O$) to α,β-unsaturated carbonyl compounds in toluene at 80 °C in 10–14 h. Finally, two groups have demonstrated[10,11] that Cu(I) in DMF, either as (10 or 100 mol%) CuCl + KOAc or 10 mol% CuOTf + PBu_3, promotes the addition of diboron reagents to α,β-unsaturated carbonyl compounds at ambient temperature. With the exception of our prior study[7] no one has investigated the primary diboration products, as only hydrolysis products have been characterised. It was of interest to conduct a more through investigation of the primary diboration products and also to develop a more active catalyst system, especially one which would be potentially amenable to inclusion of chiral ligands. To this end, we report below the development of a second generation Pt(0) catalyst system,[12] which is known to be an active hydrogenation and hydrosilylation catalyst,[13] now shown to display high activity for diboration at 5 mol% loading and ambient temperature. Furthermore, we report that this catalyst permits novel 3,4-diboration of the C=C double bond for certain α,β-unsaturated carbonyl substrates.



Scheme 1 Diboration of α,β-unsaturated carbonyl compounds and hydrolysis of the primary diboration product.

Pt(BIAN)(DMFU)[12] (BIAN = *bis*(phenylimino)acenaphthene, DMFU = dimethylfumarate, Fig. 1), a platinum(0) diimine species, was employed as the catalyst precursor at 5 mol% loading‡ and a range of α,β-unsaturated carbonyl compounds were successfully diborated using B_2pin_2 as the diboron reagent (Scheme 2). A summary of results is presented in Table 1.

In situ ^1H NMR spectroscopic analysis of reactions carried out in benzene-d_6 indicated that two distinct types of primary diborated product arise.§ Ketone substrates (R_3 = alkyl, aryl) show selectivity for the 1,4-diboration products **Xa** (O-bound boron enolates). The ^1H NMR spectra of products **1a**, **2a**, **3a** and **5a** all

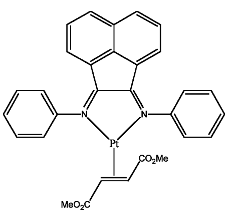
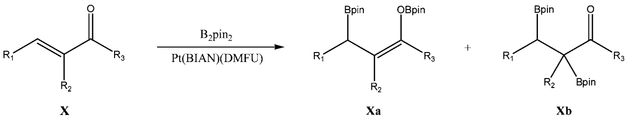


Fig. 1 Pt(BIAN)(DMFU).



Scheme 2 Regiochemistry of Pt(BIAN)(DMFU) catalysed diboration of α,β-unsaturated carbonyl compounds.

Table 1 Pt(BIAN)(DMFU)-catalysed diborations of α,β-unsaturated carbonyl substrates with *bis*-pinacolatodiboron‡

X	R_1	R_2	R_3	Conversion[a] **Xa** (%)	Conversion[a] **Xb** (%)
1	H	H	Me	100[b]	0
2	Ph	H	Me	77[c]	0
3	Ph	H	Ph	89[d]	0
4	H	Me	OMe	0	87
5	Me	H	OEt	9	59[e]
6	CO_2Me	H	OMe	0	93[e,f]

[a] Determined by ^1H NMR spectroscopy relative to the quantitative internal standard (hexamethylbenzene) after 24 h reaction time. [b] Reaction complete within 15 minutes. [c] Both *Z*-(O) and *E*-(O) isomers (3 : 1 ratio) of **2a** were identified by ^1H NMR spectroscopy. [d] Only the *Z*-(O) isomer of **3a** was observed. [e] Two diastereomers of **5b** and **6b** were identified by ^1H NMR spectroscopy (see text). [f] Reaction of the corresponding *cis*-isomer of **6** (dimethylmaleate **7**) led to the formation of the same two diastereomers of **6b** but in a different diastereomeric ratio (see text, overall conversion 83%).

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exhibit doublets (or triplets where R_1 = H) at chemical shifts consistent with olefinic protons, assignable to the proton that is R_2. Conversely, ester substrates (R_3 = alkoxyl) show selectivity for the 3,4-diboration products **Xb** (C-bound boron enolates) where B_2pin_2 effectively adds across the C=C double bond of the unsaturated ester. This is unusual as diboration of alkenes[14,15] with Pt(0)[14] is comparatively difficult except for terminal or strained cyclic systems. In addition, Onozawa and Tanaka[16] recently reported the stoichiometric 1,4-addition of a Pd–B bond to methylvinylketone **1** yielding a Pd–CH_2CH=C(Me)OBpin species. This is of interest because 3,4-diborated products cannot arise from such a pathway except *via* a subsequent rearrangement. Compound **4b** was identified by the presence of an AB doublet of doublets at 1.55 ppm. This is consistent with a CH_2 group adjacent to a chiral centre and thus, the structure is that of the 3,4-diborated product. Ethylcrotonate **5** was the only substrate to afford both 3,4- and 1,4-diborated adducts, the major products being the two diastereomers of **5b** . These were present in a 10 : 1 diastereomeric ratio. Dimethylfumarate **6** (a ligand of the catalyst precursor) is also an active substrate, with both diastereomers of **6b** present in a ratio of 3 : 1. Dimethylmaleate **7**, the *cis*-isomer of **6**, yielded both diastereomers of **6b** in a ratio of 2 : 1, the major isomer being the same as when **6** was used as the substrate. Using $Pt(NBE)_3$ (NBE = norbornene) as a catalyst precursor for these two substrates led to the formation of a mixture of **6b** and the 1,4-diborated product **6a**, which was the major product when dimethylmaleate was used as the substrate. This change in selectivity provides evidence that the BIAN ligand remains bound in the catalytic cycle.

An investigation of the hydrolysis of all of the primary diboration products was also carried out by ^1H NMR spectroscopy. It was found that B–O bonds of the 1,4-diborated products hydrolysed rapidly when the reaction mixtures were exposed to air or stoichiometric water. B–C_α bonds of the 3,4-diborated products were stable when exposed to air but hydrolysed slowly upon addition of stoichiometric water. B–C_β bonds were stable to both air and moisture. Thus, the primary diborated products **Xa** and **Xb** both hydrolyse to give a species with a boron unit β- to the carbonyl group,¶ **Xc** (Scheme 3).

The primary product of the platinum catalysed diboration of α,β-unsaturated carbonyls is highly substrate-specific and the reaction is much more complex than previously envisaged. The mechanism of the reaction, specifically the nature of the platinum-bound enolate which arises from the addition of the first Pt–B moiety across the α,β-unsaturated carbonyl, is under investigation. Finally, we note that the reaction introduces a boron atom β- to a carbonyl group whilst simultaneously generating an O- or C-bound boron enolate. The 3,4-diborated products are of particular interest as there are very few examples in the literature of boronate esters α-to a carbonyl group.[17]

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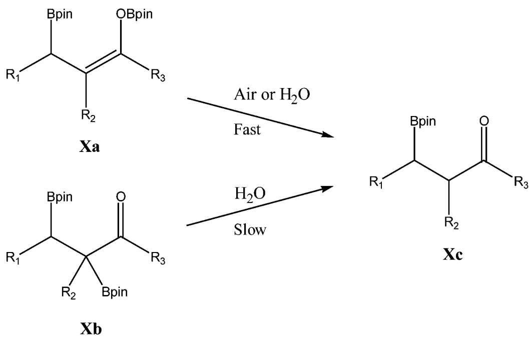

Scheme 3 Hydrolysis of primary diboration products carried out with stoichiometric quantities of H_2O.

Notes and references

‡ *General procedure*: Under an atmosphere of dry nitrogen in a double length glovebox (Innovative Technology Inc., System One) a solution of B_2pin_2 (27.8 mg, 0.11 mmol) in C_6D_6 (1 mL) was added to a solution of Pt(BIAN)(DMFU) (3.4 mg, 5 μmol), hexamethylbenzene (18 protons, 0.9 mg, 0.1/18 mmol) and substrate **X** (0.1 mmol) in C_6D_6 (1 mL). The reaction mixtures were stirred at room temperature for 24 h, after which time the solutions were transferred to NMR tubes fitted with Young's taps. Conversions were calculated by ^1H NMR spectroscopy, using hexamethylbenzene as a quantitative internal standard.

§ *Selected characterisation data*: **1a** : ^1H NMR (500 MHz, C_6D_6) δ 4.98 (td, 1 H, C=C*H*–, $^3J_{HH}$ 7.3 Hz, $^4J_{HH}$ 0.9 Hz), 1.97 (d, 2 H, CH_2Bpin, $^3J_{HH}$ 7.3 Hz), 1.87 (d 3 H, Me, $^4J_{HH}$ 0.9 Hz), *m/z* 324 $[M]^+$; **1c** : ^1H NMR (500 MHz, C_6D_6) δ 2.25 (t, 2 H, –CH_2CO, $^3J_{HH}$ 7.0 Hz), 1.61 (s, 3 H, CH_3CO), 0.97 (t, 2 H, CH_2Bpin, $^3J_{HH}$ 7.0 Hz), *m/z* 183 $[M - CH_3]^+$; **4b** : ^1H NMR (500 MHz, C_6D_6) δ 3.44 (s, 3 H, OCH_3), 1.67 (s, 3 H, CH_3), 1.55 (AB dd, 2 H, CH_2Bpin, $^2J_{HH}$ 15.7 Hz), *m/z* 339 $[M - CH_3]^+$; **6a** : ^1H NMR (500 MHz, C_6D_6) δ 5.57 (d, 1 H, CHBpinC*H*=, $^3J_{HH}$ 10.5 Hz), 5.00 (d, 1 H, C*H*BpinCH=, $^3J_{HH}$ 10.5 Hz), 3.46 (s, 3 H, C(O)CH_3), 3.16 (s, 3 H, =C(OBpin)CH_3), *m/z* 398 $[M]^+$; **6b**, major isomer: ^1H NMR (500 MHz, C_6D_6) δ 3.42 (s, 3 H, OCH_3), 3.05 (s, 1 H, C*H*Bpin), *m/z* 398 $[M]^+$; **6b**, minor isomer: ^1H NMR (500 MHz, C_6D_6) δ 3.45 (s, 3 H, OCH_3), 3.28 (s, 1 H, C*H*Bpin), *m/z* 398 $[M]^+$; **6d** : ^1H NMR (500 MHz, C_6D_6) δ 3.27 (s, 3 H, OCH_3), 2.28 (s, 2 H, CH_2Bpin), *m/z* 144 $[M]^+$.

¶ An exception to this is for substrates **6** and **7** where both boron units of the products are α- to a carbonyl group. Thus, hydrolysis results in the product which would arise from hydrogenation of the C=C double bond **6d** ($MeO_2CCH_2CH_2CO_2Me$).

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