## Experimental Section

**General**: All reactions and manipulations were carried out under an atmosphere of dry nitrogen. All organic solvents were dried, distilled and degassed before use. The palladium complexes were prepared following already reported methods.[1] Styrene, bis(catecholato)diboron and bis(pinacolato)diboron were purchased from Aldrich. NMR spectra were recorded on a Varian Gemini 300 and Mercury 400 spectrometers. Chemical shifts were reported relative to tetramethylsilane for $^{1}H$ and $BF_3$.ether for $^{11}B$, using thf-$d_8$ as solvent.

**Typical catalytic diboration of styrene**: Bis(catecholato)diboron (1.5 mmol) was added to a solution of the catalyst (5 mol%, 0.025 mmol) and NaOAc (0.5 mmol) in thf (2 mL) under argon. The solution was stirred for 5 minutes and styrene (0.5 mmol) was then added. The mixture was stirred for 4 hours at room temperature. After that time, a solution aliquot was taken from the reaction mixture and monitored by $^{1}H$ NMR from which the degree of conversion as well as the nature of the organoboron products formed in the reaction were obtained.

**NMR scale experiments. (a) [IPrCu(NCCH$_3$)]BF$_4$ (2) with catecholborane (HBcat).** Diboron $B_2cat_2$ (0.025 mmol) was dissolved in 1 mL of thf-$d_8$, in a sealable NMR tube., providing a unique signal at $^{11}B$ NMR (thf-$d_8$): 28 ppm (broad signal). Addition of freshly prepared (NHC)Pd(II)-Br, (0.025 mmol), and NaOAc generated a new signal at 13.6 ppm in $^{11}B$ NMR (thf-$d_8$).

## Computational details

All DFT calculations were carried out using the Amsterdam Density Functional (ADF2005.01) program developed by Baerends *et al*.[2] The numerical integration scheme applied for the calculations was developed by te Velde *et al*.[3] The geometry optimization procedure was based on the method reported by Versluis and Ziegler.[4] The BP86 functional described as a combination between local VWN

exchange-correlation potential with nonlocal Becke's exchange correction[5] and Perdew's correlation correction were used.[6] Relativistic corrections were introduced by scalar-relativistic Zero Order Regular Approximation (ZORA).[7] A triple-ξ plus one polarization basis set was used for all the atoms. For non-hydrogen atoms a relativistic frozen-core basis set was used, including 3d for Pd and Br, and 1s for boron, carbon, nitrogen and oxygen.

$B_2$(cat)

BE= -177,43879442 eV

| | | | |
|---|---|---|---|
| B | -1.038289364 | -0.836688935 | 1.128864374 |
| B | -1.315765329 | 0.064501127 | -0.267556478 |
| O | 0.176391575 | -1.462143995 | 1.437915893 |
| O | -1.993399497 | -1.069762117 | 2.126733482 |
| O | -2.536630146 | 0.669027580 | -0.593452048 |
| O | -0.358121360 | 0.293039029 | -1.263849874 |
| C | -2.325203986 | 1.278403612 | -1.823561721 |
| C | -1.008745945 | 1.051428223 | -2.228481491 |
| C | -3.218761672 | 2.004834088 | -2.596469005 |
| C | -2.729912170 | 2.502042456 | -3.813905722 |
| C | -1.406663477 | 2.274262584 | -4.220595090 |
| C | -0.512526248 | 1.538567726 | -3.428438188 |
| C | -1.349743130 | -1.859090975 | 3.070888760 |
| C | -0.038570029 | -2.096255968 | 2.654674064 |
| C | 0.846254212 | -2.856815013 | 3.404546489 |
| C | 0.353934777 | -3.379217233 | 4.610108757 |
| C | -0.963895033 | -3.141160947 | 5.028252285 |
| C | -1.848906180 | -2.369701148 | 4.259914167 |

| | | | |
|---|---|---|---|
| H | -4.244758144 | 2.172721456 | -2.271469380 |
| H | -3.395609523 | 3.077067365 | -4.457176181 |
| H | -1.063432042 | 2.675706798 | -5.173815545 |
| H | 0.516076626 | 1.352761511 | -3.734730078 |
| H | 1.866854041 | -3.035958166 | 3.068817376 |
| H | 1.012740947 | -3.981957009 | 5.235080537 |
| H | -1.309905700 | -3.562488058 | 5.972063340 |
| H | -2.874452551 | -2.179362467 | 4.573516397 |

3a $[Pd\text{-}NHC\text{-}Br]^+$

BE= -200,46186897

| | | | |
|---|---|---|---|
| Pd | -0.268331768 | 1.616576103 | 2.329183845 |
| C | -2.113253952 | 2.342023008 | 2.900344037 |
| N | -2.096716108 | 3.737656896 | 2.989049062 |
| C | -3.349517348 | 4.228849650 | 3.356364338 |
| C | -4.146075974 | 3.141797816 | 3.497953408 |
| N | -3.380558007 | 2.009855884 | 3.218911103 |
| C | -0.911978262 | 4.434486732 | 2.701421927 |
| N | 0.083075158 | 3.595432969 | 2.353529513 |
| C | 1.310323054 | 4.049972023 | 2.031299532 |
| C | 1.597466552 | 5.411744893 | 2.044643159 |
| C | 0.564165530 | 6.284716413 | 2.405911137 |
| C | -0.708067176 | 5.811594663 | 2.739501117 |
| N | 2.178462308 | 2.995669254 | 1.700574836 |
| N | 2.773065226 | 0.940743052 | 1.368140125 |
| C | 3.874493036 | 1.747571954 | 1.085726169 |
| C | 3.510314162 | 3.036740073 | 1.292183301 |
| C | 1.710213191 | 1.678634882 | 1.749791151 |
| H | -3.566056376 | 5.280345899 | 3.485443888 |

| | | | |
|---|---|---|---|
| H | -5.190682879 | 3.076309980 | 3.773699973 |
| H | 2.583776697 | 5.788632382 | 1.785475776 |
| H | 0.756761456 | 7.356383236 | 2.426563431 |
| H | -1.505174132 | 6.496447277 | 3.018554375 |
| H | 4.822489754 | 1.335848942 | 0.764298170 |
| H | 4.076300381 | 3.951725876 | 1.184242797 |
| C | 2.785523320 | -0.522000562 | 1.244458137 |
| H | 3.610201905 | -0.926982023 | 1.841653432 |
| H | 2.918481787 | -0.796074172 | 0.191189096 |
| H | 1.827457802 | -0.905784427 | 1.611144151 |
| C | -3.912259331 | 0.641908120 | 3.256100596 |
| H | -3.083303990 | -0.053450354 | 3.085850267 |
| H | -4.665886325 | 0.523959793 | 2.468477311 |
| H | -4.366245768 | 0.458746296 | 4.236451540 |
| Br | -0.689967717 | -0.819602434 | 2.333207288 |

3a-B2 [Pd-NHC-$(Bcat)_2$-Br]$^+$

BE= -376,90420458 eV

Pd -0.5408 1.5095 1.4612

C -2.3438 2.2359 2.2900

N -2.1248 3.4133 3.0161

C -3.3031 3.8778 3.5891

C -4.2645 3.0010 3.2243

N -3.6700 2.0148 2.4418

C -0.8407 3.9722 3.1508

N 0.0727 3.2686 2.4887

C 1.3630 3.5885 2.4954

C 1.8230 4.7088 3.1863

C 0.8658 5.4640 3.8717

C -0.4875 5.1110 3.8734

N 2.1291 2.6729 1.7509

N 2.6035 0.9302 0.5636

C 3.7948 1.6061 0.8132

C 3.5054 2.6966 1.5576

C 1.5483 1.5611 1.1281

H -3.3563 4.7653 4.2033

H -5.3204 2.9841 3.4584

H 2.8730 4.9901 3.2025

H 1.1837 6.3480 4.4237

H -1.2186 5.7020 4.4195

H 4.7450 1.2436 0.4445

H 4.1502 3.4619 1.9652

C 2.5862 -0.2927 -0.2441

H 3.5279 -0.8243 -0.0773

H 2.4872 -0.0326 -1.3047

H 1.7434 -0.9120 0.0555

C -4.4639 0.9202 1.8765

H -3.8365 0.0380 1.7672

H -4.8524 1.2144 0.8943

H -5.2938 0.7147 2.5592

B -1.1384 -0.2106 0.4600

B -0.8916 2.5455 -0.3051

O -1.2347 -1.4801 1.0388

O -1.5733 -0.2480 -0.8685

O -2.0983 3.1814 -0.6138

O 0.1162 2.8929 -1.2096

C -1.8146 3.9759 -1.7284

C -0.4800 3.8030 -2.0861

C -2.6544 4.8406 -2.4115

C -2.0858 5.5416 -3.4858

C -0.7403 5.3721 -3.8416

C 0.0959 4.4871 -3.1441

C -1.9911 -1.5602 -1.0966

C -1.7880 -2.3055 0.0583

C -2.1174 -3.6481 0.1392

C -2.6776 -4.2201 -1.0129

C -2.8790 -3.4694 -2.1789

C -2.5368 -2.1103 -2.2443

H -3.6969 4.9702 -2.1249

H -2.7056 6.2345 -4.0536

H -0.3325 5.9390 -4.6777

H 1.1419 4.3477 -3.4125

H -1.9557 -4.2268 1.0471

H -2.9606 -5.2720 -0.9977

H -3.3157 -3.9478 -3.0546

H -2.6974 -1.5207 -3.1454

Br -0.1250 0.1268 3.6983

BcatBr

BE= -90,98767728 eV

| | | | |
|---|---|---|---|
| Br | -0.99300 | -0.98379 | 1.35679 |
| B | -1.31577 | 0.06450 | -0.26756 |
| O | -2.53663 | 0.66903 | -0.59345 |
| O | -0.35812 | 0.29304 | -1.26385 |
| C | -2.32520 | 1.27840 | -1.82356 |
| C | -1.00875 | 1.05143 | -2.22848 |
| C | -3.21876 | 2.00483 | -2.59647 |
| C | -2.72991 | 2.50204 | -3.81391 |

| | | | |
|---|---|---|---|
| C | -1.40666 | 2.27426 | -4.22060 |
| C | -0.51253 | 1.53857 | -3.42844 |
| H | -4.24476 | 2.17272 | -2.27147 |
| H | -3.39561 | 3.07707 | -4.45718 |
| H | -1.06343 | 2.67571 | -5.17382 |
| H | 0.51608 | 1.35276 | -3.73473 |

3a-B [Pd-NHC-Bcat]$^{+}$

BE=-286,76458827 eV

| | | | |
|---|---|---|---|
| Pd | -0.537890892 | 1.467858331 | 1.515808382 |
| C | -2.322867363 | 2.164823474 | 2.309029700 |
| N | -2.140452286 | 3.358267426 | 3.027564803 |
| C | -3.343999235 | 3.817216922 | 3.555125467 |
| C | -4.286504683 | 2.923280627 | 3.170197868 |
| N | -3.651058909 | 1.934830562 | 2.422650137 |
| C | -0.855290508 | 3.938261693 | 3.151942495 |
| N | 0.063707018 | 3.225650714 | 2.505574148 |
| C | 1.353303642 | 3.556462826 | 2.490772171 |
| C | 1.807296943 | 4.698949541 | 3.150262021 |
| C | 0.844470467 | 5.461784865 | 3.822621744 |
| C | -0.507544575 | 5.099410113 | 3.842131985 |
| N | 2.118795951 | 2.624995377 | 1.750655908 |
| N | 2.543914583 | 0.875532513 | 0.552768344 |
| C | 3.748737607 | 1.546685748 | 0.751721131 |
| C | 3.487985721 | 2.642716257 | 1.505209991 |
| C | 1.508777195 | 1.508321140 | 1.153768744 |
| H | -3.430991388 | 4.714647782 | 4.151827152 |

| | | | |
|---|---|---|---|
| H | -5.350482493 | 2.904573773 | 3.369497348 |
| H | 2.854042973 | 4.992664466 | 3.151628436 |
| H | 1.158259032 | 6.362418079 | 4.349037144 |
| H | -1.240074793 | 5.701488112 | 4.374621192 |
| H | 4.686136522 | 1.186815636 | 0.348040434 |
| H | 4.153474321 | 3.408083753 | 1.880491940 |
| C | 2.430933423 | -0.338199351 | -0.261043276 |
| H | 3.322929561 | -0.953677946 | -0.105369982 |
| H | 2.347585602 | -0.069956496 | -1.321231930 |
| H | 1.542814795 | -0.892457616 | 0.052391390 |
| C | -4.372062517 | 0.817061751 | 1.802174760 |
| H | -3.681233066 | -0.019026393 | 1.666785448 |
| H | -4.776989741 | 1.127057436 | 0.831448944 |
| H | -5.189723451 | 0.514399534 | 2.464146577 |
| B | -1.139089475 | -0.237976831 | 0.601940033 |
| O | -1.159466901 | -1.503877259 | 1.223540047 |
| O | -1.579323382 | -0.337297414 | -0.727592416 |
| C | -1.854010124 | -1.688510684 | -0.932000029 |
| C | -1.600712611 | -2.391302621 | 0.243818137 |
| C | -1.771944888 | -3.763272364 | 0.334372038 |
| C | -2.209741602 | -4.415680512 | -0.828988475 |
| C | -2.467305851 | -3.707884356 | -2.010924535 |
| C | -2.291629569 | -2.316878003 | -2.085745674 |
| H | -1.570195883 | -4.301938942 | 1.259409545 |
| H | -2.355354110 | -5.495233187 | -0.808607785 |
| H | -2.802058571 | -4.248163407 | -2.895682424 |
| H | -2.482528784 | -1.757109155 | -3.000545468 |

3a'-σB2 [Pd-NHC-(σ-$B_2cat_2$)]$^{2+}$

BE= -366,55201423 eV

| | | | |
|---|---|---|---|
| Pd | -0.522170068 | 1.513192131 | 1.532020706 |
| C | -2.345014861 | 2.189389601 | 2.319011133 |
| N | -2.149497611 | 3.370663346 | 3.036229503 |
| C | -3.344398548 | 3.837231784 | 3.576206256 |
| C | -4.291579598 | 2.949473449 | 3.194082475 |
| N | -3.672711277 | 1.957791568 | 2.435437611 |
| C | -0.863684221 | 3.925805839 | 3.147143374 |
| N | 0.058419253 | 3.196705377 | 2.498666308 |
| C | 1.356503132 | 3.539379102 | 2.483099393 |
| C | 1.800251833 | 4.680630978 | 3.143732486 |
| C | 0.844071031 | 5.446725714 | 3.816118914 |
| C | -0.505262734 | 5.083284271 | 3.831158766 |
| N | 2.134672891 | 2.627258810 | 1.750961896 |
| N | 2.571809346 | 0.884659348 | 0.546732972 |
| C | 3.770986884 | 1.560459208 | 0.763925140 |
| C | 3.506255360 | 2.652073998 | 1.518618264 |
| C | 1.537797546 | 1.519626204 | 1.145587767 |
| H | -3.424247250 | 4.731635774 | 4.178180589 |
| H | -5.353943651 | 2.931402149 | 3.401450777 |
| H | 2.848674164 | 4.967714672 | 3.141427783 |
| H | 1.158418982 | 6.346724679 | 4.343171908 |
| H | -1.242220463 | 5.682645129 | 4.359642231 |
| H | 4.710490524 | 1.199950553 | 0.364806962 |
| H | 4.168133718 | 3.416441010 | 1.901232635 |
| C | 2.523936446 | -0.326440069 | -0.286767606 |
| H | 3.451977118 | -0.884394691 | -0.129743138 |
| H | 2.435503846 | -0.044473804 | -1.340574120 |
| H | 1.678089732 | -0.940973745 | 0.011785880 |

| | | | |
|---|---|---|---|
| C | -4.450236313 | 0.864013120 | 1.832813956 |
| H | -3.812178757 | -0.007320168 | 1.703817787 |
| H | -4.852037846 | 1.186516880 | 0.867397630 |
| H | -5.271866906 | 0.616351997 | 2.511578214 |
| B | -1.012443601 | -0.781039123 | 1.185395706 |
| B | -1.287748608 | 0.173709573 | -0.234564266 |
| O | 0.179289188 | -1.475265291 | 1.476962250 |
| O | -1.981333062 | -1.088088931 | 2.162104971 |
| O | -2.531008479 | 0.718660888 | -0.612716380 |
| O | -0.356824907 | 0.345558577 | -1.279384089 |
| C | -2.345622925 | 1.260827609 | -1.868151528 |
| C | -1.021633647 | 1.032703728 | -2.274673294 |
| C | -3.242296680 | 1.994009908 | -2.638383727 |
| C | -2.742471967 | 2.501836308 | -3.839855417 |
| C | -1.411609147 | 2.270682232 | -4.250011289 |
| C | -0.520721410 | 1.523044413 | -3.476259233 |
| C | -1.365033180 | -1.925276006 | 3.072324100 |
| C | -0.048188197 | -2.162444542 | 2.653749007 |
| C | 0.849012039 | -2.906603305 | 3.411085329 |
| C | 0.363334233 | -3.389958514 | 4.628854156 |
| C | -0.961581820 | -3.149293257 | 5.051230627 |
| C | -1.861933398 | -2.415566487 | 4.274441619 |
| H | -4.266066575 | 2.178212003 | -2.316408933 |
| H | -3.394127827 | 3.101882253 | -4.474187538 |
| H | -1.067794310 | 2.696899782 | -5.192041562 |
| H | 0.508682559 | 1.351387374 | -3.787042635 |
| H | 1.873581444 | -3.081737712 | 3.086221479 |
| H | 1.029745239 | -3.957543222 | 5.277466357 |
| H | -1.287176458 | -3.536443217 | 6.016071497 |
| H | -2.881971661 | -2.219242381 | 4.601290534 |

3a'-B2 [Pd- NHC-(Bcat)]$^{2+}$

BE= -366,13462832 eV

| | | | |
|---|---|---|---|
| Pd | -0.540841 | 1.617776 | 1.437264 |
| C | -2.314571 | 2.279337 | 2.297309 |
| N | -2.106652 | 3.373129 | 3.138424 |
| C | -3.306029 | 3.774726 | 3.716809 |
| C | -4.254683 | 2.926082 | 3.246307 |
| N | -3.633312 | 2.022654 | 2.390868 |
| C | -0.804191 | 3.903971 | 3.329393 |
| N | 0.120905 | 3.160985 | 2.716937 |
| C | 1.411019 | 3.504175 | 2.667767 |
| C | 1.869387 | 4.638440 | 3.331980 |
| C | 0.913087 | 5.397569 | 4.017842 |
| C | -0.445535 | 5.055913 | 4.022950 |
| N | 2.157216 | 2.604808 | 1.864345 |
| N | 2.517615 | 0.924030 | 0.539952 |
| C | 3.750504 | 1.496773 | 0.835703 |
| C | 3.532620 | 2.549631 | 1.663034 |
| C | 1.520141 | 1.590557 | 1.149697 |
| H | -3.388231 | 4.596917 | 4.414587 |
| H | -5.315282 | 2.882728 | 3.459737 |
| H | 2.913597 | 4.941687 | 3.312675 |
| H | 1.232236 | 6.296178 | 4.545319 |
| H | -1.175800 | 5.679446 | 4.533690 |
| H | 4.678858 | 1.099907 | 0.444959 |
| H | 4.232635 | 3.231759 | 2.126822 |
| C | 2.362778 | -0.249046 | -0.334665 |

| | | | |
|---|---|---|---|
| H | 3.231255 | -0.900727 | -0.197937 |
| H | 2.296296 | 0.072447 | -1.379908 |
| H | 1.459864 | -0.793455 | -0.046114 |
| C | -4.350358 | 0.943541 | 1.692663 |
| H | -3.660827 | 0.114570 | 1.513861 |
| H | -4.751025 | 1.316640 | 0.743825 |
| H | -5.166676 | 0.597966 | 2.334180 |
| B | -1.143380 | -0.008929 | 0.280094 |
| B | -0.948913 | 2.465082 | -0.396564 |
| O | -1.134801 | -1.219548 | 0.959143 |
| O | -1.552993 | -0.121515 | -1.034145 |
| O | -2.150590 | 3.076020 | -0.661971 |
| O | 0.059905 | 2.744389 | -1.286838 |
| C | -1.869737 | 3.856788 | -1.809107 |
| C | -0.542766 | 3.660613 | -2.181647 |
| C | -2.708081 | 4.729109 | -2.480671 |
| C | -2.136565 | 5.412817 | -3.564101 |
| C | -0.798098 | 5.218025 | -3.936325 |
| C | 0.037229 | 4.327033 | -3.246293 |
| C | -1.826858 | -1.496761 | -1.201018 |
| C | -1.576347 | -2.157914 | -0.003812 |
| C | -1.757691 | -3.522943 | 0.142146 |
| C | -2.212591 | -4.204037 | -0.997490 |
| C | -2.466170 | -3.535294 | -2.203719 |
| C | -2.276348 | -2.151258 | -2.333599 |
| H | -3.743957 | 4.880240 | -2.181607 |
| H | -2.749862 | 6.116072 | -4.125582 |
| H | -0.391905 | 5.774652 | -4.779882 |
| H | 1.079052 | 4.175786 | -3.523896 |
| H | -1.561953 | -4.034523 | 1.083694 |

| | | | |
|---|---|---|---|
| H | -2.372550 | -5.279620 | -0.940151 |
| H | -2.820626 | -4.102113 | -3.064137 |
| H | -2.471508 | -1.622192 | -3.264863 |

Bcat-OH

BE= -100.41954122 eV

| | | | |
|---|---|---|---|
| B | -1.305806 | 0.068658 | -0.255746 |
| O | -2.539987 | 0.661287 | -0.565198 |
| O | -0.347023 | 0.266628 | -1.253618 |
| C | -2.325494 | 1.256941 | -1.807746 |
| C | -1.009130 | 1.022130 | -2.215474 |
| C | -3.210784 | 1.998851 | -2.569577 |
| C | -2.722013 | 2.501217 | -3.787919 |
| C | -1.405048 | 2.263507 | -4.198970 |
| C | -0.515710 | 1.511200 | -3.412960 |
| H | -4.234035 | 2.173772 | -2.238964 |
| H | -3.384501 | 3.090066 | -4.421713 |
| H | -1.057615 | 2.670885 | -5.148016 |
| H | 0.512422 | 1.321731 | -3.719315 |
| O | -1.023481 | -0.623442 | 0.880694 |
| H | -1.789200 | -0.675588 | 1.476323 |

[Pd(NHC)-OH]+

BE= -208.02312468 eV

| | | | |
|---|---|---|---|
| Pd | -0.251744 | 1.658394 | 2.360579 |
| C | -2.092455 | 2.379049 | 2.902523 |
| N | -2.100091 | 3.774365 | 2.962084 |
| C | -3.368610 | 4.245983 | 3.298443 |
| C | -4.150217 | 3.145847 | 3.443493 |
| N | -3.356194 | 2.025428 | 3.196985 |
| C | -0.917276 | 4.476200 | 2.658454 |
| N | 0.075083 | 3.640428 | 2.302280 |
| C | 1.304071 | 4.090228 | 1.990237 |
| C | 1.593104 | 5.452610 | 2.005281 |
| C | 0.559433 | 6.324687 | 2.362019 |
| C | -0.713515 | 5.853375 | 2.699351 |
| N | 2.177516 | 3.031100 | 1.675369 |
| N | 2.746859 | 0.964979 | 1.361427 |
| C | 3.849456 | 1.755826 | 1.036690 |
| C | 3.499462 | 3.052590 | 1.231944 |
| C | 1.706992 | 1.718940 | 1.760375 |
| H | -3.610847 | 5.294658 | 3.401821 |
| H | -5.199426 | 3.069626 | 3.698427 |
| H | 2.582081 | 5.827236 | 1.753251 |
| H | 0.752197 | 7.396181 | 2.383854 |
| H | -1.508588 | 6.537923 | 2.984266 |
| H | 4.785770 | 1.334469 | 0.694047 |
| H | 4.070003 | 3.960056 | 1.090075 |
| C | 2.689430 | -0.499773 | 1.267763 |
| H | 3.415267 | -0.941474 | 1.960248 |
| H | 2.923446 | -0.806506 | 0.241903 |
| H | 1.668954 | -0.805713 | 1.533517 |

| | | | |
|---|---|---|---|
| C | -3.815459 | 0.630440 | 3.223254 |
| H | -2.966798 | -0.000067 | 2.926841 |
| H | -4.644860 | 0.508945 | 2.517132 |
| H | -4.150280 | 0.372348 | 4.234578 |
| O | -0.579862 | -0.331794 | 2.419205 |
| H | -0.341212 | -0.594333 | 3.331563 |

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