Supporting Information

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Chiral Boron-Bridged Bisoxazoline (borabox) Ligands:
Structure and Reactivity of Pd and Cu Complexes

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8d. (S)-2-Amino-1,1,3-triphenylpropan-1-ol (1.49 g, 4.91 mmol) and ethyl formimidate hydrochloride (544 mg, 4.97 mmol) were refluxed in CH₂Cl₂ (100 mL) overnight. After cooling NEt₃ (3.4 mL, 24 mmol) was added and the reaction mixture was washed with sat. aq. NaHCO₃-solution (60 mL). The organic phase was dried over Na₂SO₄ and after removal of volatiles the crude product was obtained as a white solid (1.56 g). The crude product was extracted first with EtOH and subsequently with hexanes. After concentration, CH₂Cl₂ was added to the residue and insoluble compounds were removed by filtration over Celite®. Removal of volatiles afforded an off-white solid (1.10 g, 75%), which was used in the next step without further purification.

NMR (500 MHz, CD₂Cl₂): δ = 7.49 (m, 2H, arom CH (A) ortho), 7.42 (m, 2H, arom CH (A) meta), 7.38-7.29 (m, 4H, arom CH (B) meta, para, arom CH (A) para), 7.26 (m, 2H, arom CH (C) meta), 7.21 (m, 2H, arom CH (B) ortho), 7.19 (m, 1H, arom CH (C) para), 7.14 (m, 2H, arom CH (C) ortho), 7.09 (d, 3J(H,H) = 2.1 Hz, N=CH), 4.91 (ddd, 3J(H,H) = 10.8, 4.3 Hz, 4J(H,H) = 2.1 Hz, 1H, oxa), 2.57 (dd, 2J(H,H) = 14.0 Hz, 3J(H,H) = 4.3 Hz, 1H, PhCH₁H), 2.22 (dd, 2J(H,H) = 14.0 Hz, 3J(H,H) = 10.8 Hz, 1H, PhCH₂H);

13C NMR (CD₂Cl₂, 126 MHz): δ = 153.4 (N=CH), 144.5 (arom C (A) ipso), 140.9 (arom C (B) ipso), 139.9 (arom C (C) ipso), 129.7 (arom CH (C) ortho), 129.0 (arom CH (A) meta), 128.7 (arom CH (C) meta), 128.6 (arom CH (A) para), 128.5 (arom CH (B) meta, the assignment was not unambiguous for this signal), 128.2 (arom CH (B) ortho), 127.0 (arom CH (A) ortho), 126.7 (arom CH (C) para), 92.2 (Ph₂C), 75.7 (oxa CH), 41.0 (PhCH₂); IR: 3057, 3043, 3028, 2964, 2905, 1634, 1491, 1447, 1259, 1059, 1078, 962, 758, 750, 735, 692; MS (FAB) m/z (%): 314 ([M⁺ + H]+, 58), 91 (100).

(7ax)-H. Yield 65%; [α]D²⁰ = −74 (c = 0.39, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃): δ = 13.51 (bs, 1H, NHN), 4.37 (dd, 3J(H,H) = 9.7 Hz, ²J(H,H) = 8.9 Hz, 2H, oxa CHH), 4.06 (dd, ²J(H,H) = 8.9 Hz, ³J = 7.7 Hz, 2H, oxa CHH), 3.84 (bm, 2H, oxa CH), 1.69 (m, 2H, CH(CH₃)₂), 0.99 (d, ³J(H,H) = 6.9 Hz, 6H, CH(CH₃)(CH₃), 0.93 (d, ³J(H,H) = 6.6 Hz, 6H, CH(CH₃)(CH₃)), 0.65 (t, ³J(H,H) = 7.6 Hz, 6H, CH₂CH₃), 0.43 (bq, ³J(H,H) = 7.6 Hz, 4H, CH₂CH₃); ¹³C NMR (126 MHz, CDCl₃): δ = 198.9 (b, N=C), 71.4 (oxa CH₂), 67.1 (oxa CH), 32.7 (CH(CH₃)₂), 18.7 (CH(CH₃)(CH₃), 18.5 (CH(CH₃)(CH₃)), 14.1 (b, CH₂CH₃), 11.8 (CH₂CH₃); ¹¹B NMR (161 MHz, CDCl₃): δ = −15.7 (s); IR: 2955, 2935, 2899, 2874, 2860, 2818, 1585, 1466, 1414, 1312, 1165, 1032, 962, 932; MS (FAB) m/z (%): 305 (5), 295 ([M⁺ + H]+, 100), 265 ([M⁺ + Et]+, 8), 182 ([M⁺ - oxa], 17); elemental analysis caled (%) for C₁₆H₃₁N₂O₂B₁ (294.2): C 65.31, H 10.62, N 9.52; found: C 65.38, H 10.35, N 9.58.
(7ay)-H. Yield: 63%; $R_t = 0.43$; $[\alpha]_D^{20} = -66$ (c = 0.11, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 10.76$ (bs, 1H, NHN), 7.32 (m, 4H, arom CH meta), 7.21 (m, 4H, arom CH ortho), 7.14 (m, 2H, arom CH para), 4.40 (m, 2H, oxa), 4.11 (m, 2H, oxa), 3.86 (m, 2H, oxa), 1.78 (m, 2H, CH(CH$_3$)$_2$), 1.05 (d, $^3$J(H,H) = 6.8 Hz, 6H, CH$_3$), 0.96 (d, $^3$J(H,H) = 6.8 Hz, 6H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ C ipso and N=C not detected, 133.8 (arom CH meta), 127.1 (arom CH ortho), 125.2 (arom CH para), 72.1 (oxa), 67.3 (oxa), 32.9 (CH(CH$_3$)$_2$), 18.9 (CH$_3$), 18.8 (CH$_3$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -13.5$ (s); IR: 2954, 2877, 1581, 1465, 1411, 1311, 1272, 1218, 1164, 1033, 964, 933, 725; MS (FAB) m/z (%): 391 ([M$^+$ + H], 100), 278 ([M$^+$ − oxa], 58); elemental analysis calcd (%) for C$_{24}$H$_{31}$BN$_2$O$_2$ (390.33): C 73.85, H 8.00, N 7.18; found: C 73.75, H 7.91, N 7.15.

(7az)-H. Yield 45%; $[\alpha]_D^{20} = -47$ (c = 0.34, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ NH was not detected, 7.68 (b, 6H, arom CH), 4.45 (dd, $^3$J(H,H) = 10.1 Hz, $^1$J(H,H) = 9.1 Hz, 2H, oxa CHH), 4.18 (dd, $^2$J(H,H) = 9.1 Hz, 7.9 Hz, 2H, oxa CHH), 4.01 (ddd, $^1$J(H,H) = 10.1 Hz, 7.9 Hz, 6.3 Hz, 2H, oxa CH), 1.82 (m, 2H, CH(CH$_3$)$_2$), 1.03 (d, $^3$J(H,H) = 6.6 Hz, 6H, CH$_3$), 0.98 (d, $^3$J(H,H) = 6.9 Hz, 6H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 191.7$ (b, N=C), 149.8 (b, arom C ipso to B), 133.4 (m, arom CH ortho to B), 129.9 (bq, $^2$J(C,F) $\approx$ 33 Hz, arom C ipso to CF$_3$), 124.0 (q, $^1$J(C,F) = 273 Hz, CF$_3$), 119.8 (sep, $^3$J(C,F) = 4 Hz arom CH para to B), 72.3 (oxa CH$_2$), 67.3 (oxa CH), 32.4 (CH(CH$_3$)$_2$), 18.6 (CH$_3$), 18.2 (CH$_3$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -14.0$ (s); IR: 2964, 2932, 2880, 1599, 1418, 1358, 1275, 1117, 964, 941, 893, 841, 708, 681; MS (FAB) m/z (%): 663 ([M$^+$ + H], 100), 550 ([M$^+$ − oxa], 21); elemental analysis calcd (%) for C$_{28}$H$_{27}$BF$_2$N$_2$O$_2$ (662.3): C 50.78, H 4.11, N 4.23; found: C 50.71, H 4.35, N 4.32.

(7bw)-H. Yield: 51%; $R_t = 0.39$; $[\alpha]_D^{20} = -35$ (c = 0.11, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 13.40$ (bs, 1H, NHN), 4.30 (m, 2H, oxa), 4.09 (m, 2H, oxa), 1.62-1.33 (m, 8H, Cy), 1.19-0.60 (m, 14H, Cy), 0.91 (s, 18H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = (N$ C not detected) 70.5 (oxa), 69.3 (oxa), 33.0 (C(CH$_3$)$_3$), 31.7 (Cy), 31.4 (Cy), 29.1 (Cy), 27.9 (Cy), 25.9 (C(CH$_3$)$_3$), $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -13.5$ (s); IR: 2954, 2908, 2839, 1581, 1473, 1442, 1404, 1203, 1149, 1018, 964, 856, 709; MS (FAB) m/z (%): 431 ([M$^+$ + H]', 100), 222 ([M$^+$ − oxa − Cy + H], 16); Elemental analysis calcd (%) for C$_{26}$H$_{47}$BN$_2$O$_2$ (430.48): C 72.54, H 11.00, N 6.51; found: C 72.40, H 10.80, N 6.36.

(7bx)-H. Yield: 65%; $[\alpha]_D^{20} = -80$ (c = 0.11, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 9.39$ (bs, 1H, NHN), 4.29 (dd, $^3$J(H,H) = 10.3 Hz, $^2$J(H,H) = 9.1 Hz, 2H, oxa CHH), 4.13 (dd, $^2$J(H,H) = 9.1 Hz, $^3$J(H,H) = 7.7 Hz, 2H, oxa CHH), 3.82 (dd, $^1$J(H,H) = 10.3 Hz, 7.7 Hz, 2H, oxa CH), 0.89 (s, 18H, C(CH$_3$)$_3$), 0.66 (t, $^3$J(H,H) = 7.7 Hz, 6H, CH$_2$CH$_3$)$_3$, 0.38 (bm, 4H, CH$_2$CH$_3$)$_3$; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 198.7$ (b, N=C), 70.7 (oxa CH), 69.5 (oxa CH$_2$), 33.1 (C(CH$_3$)$_3$), 25.6 (C(CH$_3$)$_3$), 14.4 (bm, CH$_2$CH$_3$)$_3$, 12.0 (CH$_2$CH$_3$)$_3$; $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -15.7$ (s); IR: 2947, 2869, 2815, 2360, 1589, 1473, 1411, 1365, 1319, 1288, 1211, 1164, 1018, 964, 933, 848; MS (FAB) m/z (%): 323 ([M$^+$ + H], 100), 196 ([M$^+$ − oxa], 8); elemental analysis calcd (%) for C$_{18}$H$_{35}$BN$_3$O$_2$ (322.29): C 67.08, H 10.95, N 8.69; found: C 67.21, H 10.93, N 8.74.
(7by)-H. Yield: 72%; $R_f = 0.46$; $[\alpha]_D^{20} = -89$ ($c = 0.11$, CH$_2$Cl$_2$); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 13.62$ (bs, 1H, NHN), 7.35 (m, 4H, arom CH meta), 7.23 (m, 4H, arom CH ortho), 7.16 (m, 2H, arom CH para), 4.32 (m, 2H, oxa), 4.21 ('t', $J$(H,H) = 8.0 Hz, 2H, oxa), 3.90 ('t', $J$(H,H) = 8.0 Hz, 2H, oxa), 0.98 (s, 18H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ arom C ipso not detected, 194.5 (very broad signal, N=C), 134.0 (arom CH meta), 127.2 (arom CH ortho), 125.2 (arom CH para), 70.8 (oxa), 70.1 (oxa), 33.4 (C(CH$_3$)$_3$), 25.8 (CH$_3$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -13.4$ (s); IR: 2954, 2869, 2360, 1581, 1473, 1411, 1365, 1288, 1211, 1164, 1033, 964, 848, 702; MS (FAB) $m/z$ (%): 419 ([M + H$^+$]), 100), 292 ([M$^+$ – oxa], 55); elemental analysis calc'd (%) for C$_{26}$H$_{33}$BN$_2$O$_2$ (418.38): C 74.64, H 8.43, N 6.70; found: C 74.41, H 8.52, N 6.83.

(7bz)-H. Yield: 89%; $[\alpha]_D^{20} = -42$ ($c = 0.11$, CH$_2$Cl$_2$); $R_f = 0.31$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 12.62$ (bs, 1H, NHN), 7.67 (m, 6H, arom CH), 4.37 (dd, $J$(H,H) = 10.4, 9.5 Hz, 2H, oxa), 4.28 (dd, $J$(H,H) = 9.5, 7.7 Hz, 2H, oxa), 3.98 (dd, $J$(H,H) = 10.4, 7.7 Hz, 2H, oxa), 0.97 (s, 18H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ = (arom C ipso to B, CF$_3$ and N=C not detected) 133.4 (arom CH ortho to B), 119.9 (arom CH para to B), 70.9 (oxa), 70.6 (oxa), 33.4 (C(CH$_3$)$_3$), 25.5 (CH$_3$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -13.1$ (s); $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta = -63.2$ (s); IR: 2962, 2908, 1604, 1481, 1357, 1272, 1118, 964, 894, 840, 709, 678. elemental analysis calc'd (%) for C$_{30}$H$_{31}$BF$_{12}$N$_2$O$_2$ (690.37): C 52.19, H 4.53, N 4.06; found: C 52.33, H 4.61, N 4.11.

(7cx)-H. The crude product was directly applied to column chromatography over silica without previous separation from LiCl by extraction with benzene. Yield: 78%; $R_f = 0.30$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 10.31$ (bs, 1H, NHN), 7.31 (m, 4H, arom CH meta), 7.25 (m, 2H, arom CH para), 7.17 (m, 4H, arom CH ortho), 4.35 (dd, $J$(H,H) = 9.2 Hz, 2H, oxap CH), 3.93 (dd, $J$(H,H) = 9.2 Hz, 2H, oxap CH), 4.11 (dd, $J$(H,H) = 8.6 Hz, 2H, oxap CH), 2.88 (dd, $J$(H,H) = 13.7 Hz, 3H, $J$(H,H) = 6.7 Hz, 2H, PhCH$_2$), 2.70 (dd, $J$(H,H) = 13.7 Hz, 3H, $J$(H,H) = 7.3 Hz, 2H, PhCH$_2$), 0.65 (bt, $J$(H,H) = 7.6 Hz, 6H, CH$_3$), 0.44 (m, 4H, CH$_2$CH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 198.6$ (N=C), 137.4 (arom C ipso), 129.1 (arom CH ortho), 128.6 (arom CH meta), 126.8 (arom CH para), 72.8 (oxa CH$_2$), 62.3 (oxa CH), 42.2 (PhCH$_2$), 14.5 (b, CH$_2$CH$_3$), 11.9 (CH$_3$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -15.6$ (s); IR: 3140, 3032, 2932, 2893, 2854, 2824, 1566, 1488, 1450, 1396, 1288, 1203, 1157, 1026, 1003, 895, 748, 733, 702; MS (FAB) $m/z$ (%): 391 (100, [M$^+$ + H$^+$]), 230 ([M$^+$ – oxa], 18); elemental analysis calc'd (%) for C$_{26}$H$_{33}$BN$_2$O$_2$ (390.33): C 73.85, H 8.01, N 7.18; found: C 73.74, H 7.85, N 7.03.

(7cy)-H. Yield 31%; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 10.54$ (bs, 1H, NHN), 7.35-7.10 (m, 20H, arom CH), 4.36-4.24 (m, overlayed signals, 4H, oxap CH, oxa CHH), 4.11 (m, 2H, oxa CHH), 2.88 (dd, $J$(H,H) = 13.8 Hz, 3H, $J$(H,H) = 5.3 Hz, 2H, PhCH$_2$), 2.79 (dd, $J$(H,H) = 13.8 Hz, 3H, $J$(H,H) = 7.3 Hz, 2H, PhCH$_2$); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 194.7$ (b, N=C), 148.6 (b, arom C ipso to B), 137.0 (arom C ipso to CH$_2$), 133.8, 129.2, 128.7, 127.1, 126.9, 125.3 (arom CH), 73.2 (oxa CH$_2$), 62.2 (oxa CH), 41.5 (PhCH$_2$); $^{11}$B NMR (161 MHz, CDCl$_3$): $\delta = -13.5$ (s); IR: 3065, 3026, 2999, 2914, 1583, 1489, 1454, 1414, 1296, 1165, 964, 727, 698; MS (FAB): $m/z$ (%): 487 ([M$^+$ + H$^+$], 84), 409 ([M$^+$ – O]$_2$).
Ph], 8), 326 ([M⁺ – oxa], 76), 91 (100); elemental analysis calcd (%) for C32H31B1N2O2 (486.4): C 79.02, H 6.42, N 5.76; found: C 78.81, H 6.44, N 5.59.

(7cz)-H. The crude product was directly applied to column chromatography over silica without previous separation from LiCl by extraction with benzene. Yield: 44%; Rf = 0.34; ¹H NMR (500 MHz, CDCl₃): δ = 8.82 (bs, 1H, NHN), 7.68 (bs, 2H, arom CH para to B), 7.60 (bs, 4H, arom CH ortho to B), 7.29 (m, 4 H, arom CH meta to CH₂), 7.24 (m, 2H, arom CH para to CH₂), 7.14 (m, 4H, arom CH ortho to CH₂), 4.44 (m, 4H, oxa C H, oxa CH₂H), 4.20 (m, 2H, oxa CH), 2.86 (m, 4H, PhC H₂); ¹³C NMR (126 MHz, CDCl₃): δ = 191.8 (b, N=C), 149.7 (b, arom C ipso to B), 136.2 (arom C ipso to CH₂), 133.3 (b, arom CH ortho to B), 130.0 (q, ¹²J(C,F) = 272 Hz, CF₃), 129.0 (arom CH ortho to CH₂), 128.7 (arom CH meta to CH₂), 127.2 (arom CH para to CH₂), 124.0 (q, ¹¹J(C,F) = 4 Hz, arom CH para to B), 119.9 (sep, ³J(C,F) = 4 Hz, arom CH para to B), 62.3 (oxa CH), 41.2 (PhC H₂); ¹¹B NMR (161 MHz, CDCl₃): δ = −14.1 ppm; IR: 2962, 2924, 1597, 1497, 1473, 1450, 1358, 1273, 1119, 964, 887, 841, 748, 702; MS (FAB) m/z (%): 759 ([M⁺ + H], 75), 667 ([M⁺ – CH₂Ph], 5), 598 ([M⁺ – oxa], 17); elemental analysis calcd (%) for C₃6H₂₇BF₁₂N₂O₂ (758.20): C 57.01, H 3.59, N 3.69; found: C 57.04, H 3.73, N 3.65.

(7dx)-H. This ligand was purified by column chromatography using toluene as eluent. The product was obtained as a white solid. Yield: 23%;

¹H NMR (500 MHz, C₆D₆): δ = 7.51 (m, 4H, arom CH (A) ortho), 7.37 (m, 4H, arom CH (B) ortho), 7.12 (m, 4H, arom CH (A) meta), 7.07-6.98 (m, 12H, arom CH (A) para, arom CH (B) meta, arom CH (C) meta, arom CH (C) para), 6.96 (m, 2H, arom CH (B) para), 6.82 (m, 4H, arom CH (C) ortho), 5.66 (bs, 1H, NHN), 4.77 (dd, ³J(H,H) = 9.6, 5.3 Hz, 2H, oxa), 2.38 (dd, ²J(H,H) = 13.7 Hz, ³J(H,H) = 5.3 Hz, 2H, PhCH₂), 2.25 (dd, ²J(H,H) = 13.7 Hz, ³J(H,H) = 9.6 Hz, 2H, PhCH₂), 1.50-1.30 (m, 4H, C H₂CH₃), 1.19 (t, ³J(H,H) = 7.7 Hz, 6H, CH₃); ¹³C NMR (126 MHz, C₆D₆): δ = 197.5 (N=C), 144.4 (arom C (A) ipso), 140.4 (arom C (B) ipso), 138.4 (arom C (C) ipso), 129.5 (arom CH (C) ortho), 128.6, 128.5, 128.4, 127.8 (overlaid by solvent signal, arom CH), 127.7 (overlaid by solvent signal, arom CH (B) para), 127.4 (arom CH (B) ortho), 26.8 (arom CH (A) ortho), 126.5 (arom CH (C) para), 93.9 (Ph₂C), 70.6 (oxa CH), 41.3 (PhCH₂), 15.1 (b, CH₂CH₃), 12.8 (CH₃); Note: Phenyl ring A and B differentiated by NOE between benzylic protons and ortho protons of ring B and NOE between oxa CH and ortho protons of ring A. The ipso-carbon of phenyl ring C was assigned by HMBC-contact with benzylic protons; ¹¹B (C₆D₆, 161 MHz): δ = −15.1 ppm; IR: 3064, 3027, 2933, 2895, 2872, 2857, 2818, 1600, 1569, 1490, 1452, 1377, 1191, 1183, 1171, 1073, 1036, 838,
737, 694; MS (FAB) m/z (%): 695 ([M⁺ + H], 87), 382 ([M⁺ – oxa], 13), 354 ([M⁺ – oxa – Et + H], 16); elemental analysis calcd (%) for C₄₈H₄₇BN₂O₂ (694.7): C 82.99, H 6.82, N 4.03; found: C 82.80, H 6.71, N 4.01.

(7ex)-H. Note: Lithiation and addition of XBR₂ for ligands 7ex and 7ey were carried out at −100 °C. After stirring at this temperature overnight work up was performed as usual. Yield: 5%; Req = 0.31; [α]D²⁰ = −35 (c = 0.11, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.36 (m, 4H, arom CH meta), 7.30 (m, 2H, arom CH para), 7.23 (m, 4H, arom CH ortho), 5.09 (dd, 3J(H,H) = 10.1 Hz, 3J(H,H) = 7.3 Hz, 2H, oxo CH), 4.72 (dd, 2J(H,H) = 10.1 Hz, ³J(H,H) = 8.8 Hz, 2H, oxo CH), 4.19 (dd, 3J(H,H) = 8.8, 7.3 Hz, 2H, oxo CH), 0.84 (t, 3J(H,H) = 7.6 Hz, 6H, CH₃), 0.62 (q, 3J(H,H) = 7.6 Hz, 4H, CH₂CH₃); ¹³C NMR (126 MHz, CDCl₃): δ = (N=C not detected) 141.2 (arom C ipso), 129.0 (arom CH meta), 126.1 (arom CH ortho), 76.1 (oxa), 64.8 (oxa), 14.8 (CH₂CH₃), 12.3 (CH₃); ¹¹B NMR (161 MHz, CDCl₃): δ = −15.3 (s); IR: 2933, 2360, 1545, 1384, 1284, 1149, 749, MS (FAB) m/z (%): 363 ([M⁺ + H], 100), 216 ([M⁺ – oxa], 19).

(7ey)-H. Yield: 58%; ¹H NMR (500 MHz, CDCl₃): Req = 0.13; [α]D²⁰ = −91 (c = 0.28, CH₂Cl₂); δ = 8.59 (bs, 1H, NHN), 7.49 (m, 4H, arom CH), 7.34 (m, 10H, arom CH), 7.23 (m, 6H, arom CH), 5.13 (dd, 3J(H,H) = 10.2 Hz, ³J(H,H) = 9.1 Hz, 2H, oxa CH), 4.73 (dd, 2J(H,H) = 10.2 Hz, ³J(H,H) = 9.1 Hz, 2H, oxa CH), 4.23 (dd, 3J(H,H) = 9.1, 7.6 Hz, 2H, oxa CH); ¹³C NMR (126 MHz, CDCl₃): δ = (arom C ipso to B not detected) 195.9 (N=C), 140.8 (arom C ipso to oxo CH), 134.0, 129.1, 128.3, 127.4, 125.6 (arom CH), 76.5 (oxa), 64.7 (oxa); ¹¹B NMR (161 MHz, CDCl₃): δ = −13.1 (s); IR: 2962, 2903, 2360, 1525, 1484, 1382, 1158, 803, 700; MS (FAB) m/z (%): 459 ([M⁺ + H], 100), 312 ([M⁺ – oxa], 79); elemental analysis calcd (%) for C₃₀H₂₇BN₂O₂ (458.37): C 78.61, H 5.94, N 6.11; found: C 78.46, H 6.10, N 5.98.

(7fy)-H. The crude product was directly applied to column chromatography over silica without previous separation from LiCl by extraction with benzene. Yield 19%. ¹H NMR (500 MHz, CDCl₃): δ = 10.41 (bs, 1H, NHN), 7.32 (m, 4H, arom CH ortho), 7.22 (m, 4H, arom CH meta), 7.15 (m, 2H, arom CH para), 4.46 (dd, 3J(H,H) = 9.5 Hz, ³J(H,H) = 8.8 Hz, 2H, oxa CH), 4.14 (3J(H,H) = 9.5 Hz, 8 Hz, 6H, oxa CH), 3.97 (dd, 3J(H,H) = 8.8 Hz, ³J(H,H) = 7.9 Hz, not fully resolved, 2H, oxa CH), 1.82 (m, 2H, CH(CH₃)₂), 1.62 (dd, 3J(H,H) = 13.6 Hz, ³J(H,H) = 8.2, 6.3 Hz, 2H, CH₂CH(CH₃)₂), 1.43 (3J(H,H) = 13.6 Hz, ³J(H,H) = 7.9, 6.0 Hz, 2H, CH₂CH(CH₃)₂); ¹¹B NMR (161 MHz, CDCl₃): δ = −13.6 (s); IR: 3067, 3042, 2997, 2955, 2928, 2870, 1583, 1468, 1416, 1290, 1267, 1167, 972, 945, 727, 700; MS (FAB): m/z (%): 419 ([M⁺ + H], 100), 341 ([M⁺ – Ph], 7), 292 ([M⁺ – oxa], 74), 165 ([M⁺ – 2 oxa – H], 21); elemental analysis calcd (%) for C₂₆H₃₅BN₂O₂ (418.38): C 74.64, H 8.43, N 6.70; found: C 74.53, H 8.44, N 6.67.
10ax. Crystallization from EtOH/H$_2$O yielded a white solid (17 mg, 22%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 5.54$ (‘ddt’, $^3$J(H,H) = 12.4, 12.0, 6.9 Hz, 1H, HC(10)), 4.09 (dd, overlayed by signal at 4.07 ppm, $^2$J(H,H) = 8.8 Hz, $^3$J(H,H) = 3.9 Hz, 1H, HHC(5('i) trans to HC(4) or HC(4'))), 4.07 (dd, overlayed by signal at 4.09 ppm, $^2$J(H,H) = 8.8 Hz, $^3$J(H,H) = 4.0 Hz, 1H, HHC(5('i) trans to HC(4) or HC(4'))), 3.90 (dd, $^3$J(H,H) = 9.6 Hz, 2$^J$(H,H) = 8.8 Hz, 1H, HHC(5('i) cis to HC(4) or HC(4')), 3.84 (dd, $^3$J(H,H) = 9.6, 4.0, 3.0 Hz, 1H, HC(4')), 3.73 (ddd, $^3$J(H,H) = 9.6, 3.9, 3.0 Hz, 1H, HC(4')), 3.71 (‘dd’, $^3$J(H,H) = 6.9 Hz, $^4$J(H,H) = 2.3 Hz, HHC(11) syn), 3.50 (‘dd’, $^3$J(H,H) = 6.9 Hz, $^4$J(H,H) = 2.3 Hz, HHC(9) syn), 2.89 (‘d’, $^3$J(H,H) = 12.4 Hz, 1H, HHC(11) anti), 2.83 (‘d’, $^3$J(H,H) = 12.0 Hz, 1H, HHC(9 anti)), 2.01 (qqd, $^3$J(H,H) = 7.0, 6.8, 3.0 Hz, 1H, HC(6)), 1.86 (qqd, $^3$J(H,H) = 7.0, 6.8, 3.0 Hz, 1H, HC(6')), 0.89 (d, $^3$J(H,H) = 7.0 Hz, 3H, H$_2$C(7)), 0.88 (d, $^3$J(H,H) = 7.0 Hz, 3H, H$_2$C(7')), 0.73 (d, $^3$J(H,H) = 6.8 Hz, 3H, H$_2$C(8)), 0.72 (t, $^3$J(H,H) = 7.7 Hz, 3H, CH$_2$CH$_3$), 0.65 (d, $^3$J(H,H) = 6.8 Hz, 3H, H$_2$C(8')), 0.62 (t, $^3$J(H,H) = 7.7 Hz, 3H, CH$_2$CH$_3$), 0.41-0.23 (m, 4H, CH$_2$CH$_3$); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta = 196.3$ (b, C(2), C(2')), 114.5 (C(10)), 74.7 (2C, C(4), C(4')), 66.5, 66.4 (C(5), C(5')), 59.5 (C(11)), 55.7 (C(9)), 31.0 (2C, C(6), C(6')), 19.7, 19.6 (C(7), C(7')), 16.6 (bm, CH$_2$CH$_3$), 14.5 (C(8')), 14.4 (C(8)), 12.3 (CH$_2$CH$_3$); $^{11}$B NMR (161 MHz, CD$_2$Cl$_2$): $\delta = -15.7$ (s).

10az. Crystallization of the crude product from EtOH/H$_2$O yielded a colorless microcrystalline powder (17 mg). Solvents were evaporated from the mother liquor and the residue was purified by column chromatography (silica gel, hexanes/EtOAc/NEt$_3$ = 20/2/1). The chromatographed batch obtained from the mother liquor of the first crystallization was then crystallized by layering an ethanolic solution of the complex with water in a NMR-tube. The crystals obtained were suitable for X-ray diffraction (12 mg; combined yield of the two crystallizations: 29 mg, 38%).
\[ \text{H NMR (500 MHz, CD}_2\text{Cl}_2): \delta = 7.74 \text{ (bs, 2H, arom CH ortho to B), 7.66 (bs, 1H, arom CH para to B), 7.63 (bs, 3H, arom CH), 5.57 ('ddt', }^3\text{J(H,H) = 12.4, 12.0, 6.9 Hz, 1H, HC(10))}, 4.11 \text{ (dd, }^2\text{J(H,H) = 9.2 Hz, }^3\text{J(H,H) = 4.5 Hz, 1H, HHC(5) trans to HC(4))}, 4.08 \text{ (m, 2H, H}_2\text{C(5'))}, 4.03 \text{ (t, }^2\text{J(H,H) = 9.2 Hz, }^3\text{J(H,H) = 4.5 Hz, 1H, HC(5) cis to HC(4))}, 4.00 \text{ (dd, }^3\text{J(H,H) = 7.3, 6.7, 3.1 Hz, 1H, HC(4'))}, 3.90 \text{ (dd, }^3\text{J(H,H) = 9.5, 4.5, 3.1 Hz, 1H, HC(4))}, 3.81 \text{ ('dd', }^3\text{J(H,H) = 6.9 Hz, }^4\text{J(H,H) = 2.2 Hz, 1H, HHC(11) syn), 3.65 ('dd', }^3\text{J(H,H) = 6.9 Hz, }^4\text{J(H,H) = 2.2 Hz, 1H, HHC(9) syn), 2.98 ('d', }^3\text{J(H,H) = 12.4 Hz, 1H, HHC(11) anti), 2.91 ('d', }^3\text{J(H,H) = 12.0 Hz, 1H, HHC(9) anti), 2.03 \text{ (qqd, }^3\text{J(H,H) = 7.1, 6.8, 3.1 Hz, 1H, HC(6))}, 1.91 \text{ (qqd, }^3\text{J(H,H) = 7.1, 6.8, 3.1 Hz, 1H, HC(6'))}, 0.87 \text{ (d, }^3\text{J(H,H) = 7.1 Hz, 3H, H}_3\text{C(7))}, 0.86 \text{ (d, }^3\text{J(H,H) = 7.1 Hz, 3H, H}_3\text{C(7'))}, 0.45 \text{ (d, }^3\text{J(H,H) = 6.8 Hz, 3H, H}_3\text{C(8))}, 0.39 \text{ (d, }^3\text{J(H,H) = 6.8 Hz, 3H, H}_3\text{C(8'))}; \]

\[ \text{13C NMR (126 MHz, CD}_2\text{Cl}_2): \delta = 189.8 \text{ (C(2), C(2'))}, 154.0 \text{ (b, 2 C, arom C ipso to B), 134.3 (4 C, arom CH ortho to B), 129.9, 129.8 (2 q, }^2\text{J(C,F) ≈ 33 Hz, 2 x 2 C, arom C ipso to CF}_3), 124.9 \text{ (2 q, }^1\text{J(C,F) ≈ 272 Hz, 2 x 2 C, CF}_3), 119.6 \text{ (2 sep, overlayed signals, 2 C, }^2\text{J(C,F) = 4 Hz, arom CH para to B), 115.7 (C(10)), 74.6, 74.5 (C(4), C(4')), 67.4 (2 C, C(5), C(5'))}, 60.5 (C(11)), 57.6 (C(9)), 31.2 (C(6)), 31.2 (C(6'))}, 19.4, 19.3 \text{ (C(7), C(7'))}, 14.0 (2C, C(8), C(8')); \]

\[ \text{11B NMR (161 MHz, CD}_2\text{Cl}_2): \delta = -13.1 \text{ (s); IR: 2964, 2937, 2898, 2877, 1597, 1481, 1465, 1355, 1272, 1180, 1145, 1120, 1105, 977, 893, 680; MS (FAB): m/z (%): 809 ([M⁺ + H]), 663 ([M⁺ – PdC}_3\text{H}_5 + 2H], 16), 550 ([M⁺ – PdC}_3\text{H}_5 – oxa + H], 7); elemental analysis calc (%) for C}_3\text{H}_3\text{N}_2\text{O}_2\text{B}_1\text{F}_1\text{Pd}_1 (808.8): C 46.0, H 3.86, N 3.46; found: C 46.0, H 3.89, N 3.50.} \]

**12a.** To a solution of ligand 6a (76.8 mg, 288 μmol) and [Pd(C}_3\text{H}_5\text{Cl}_2] (52.8 mg, 144 μmol) in CH}_2\text{Cl}_2 (3 mL) was added a solution of AgPF}_6 (74.0 mg, 293 μmol) in THF (2 mL). After 10 minutes the reaction mixture was filtered over Celite®, the volatiles were removed and the remaining solid was redissolved in CH}_2\text{Cl}_2. The organic phase was washed with water and dried over Na}_2\text{SO}_4. The product was isolated as a colorless solid after removal of volatiles in 83% yield (134 mg).
1H NMR (500 MHz, CD₂Cl₂, 295 K): [α]D = 58 (c = 0.80, CH₂Cl₂); δ = 5.72 (′ddt′, 3J(H,H) = 12.6, 12.2, 7.0 Hz, 1H, HC(10)), 4.47 (dd, 2J(H,H) = 9.3 Hz, 3J(H,H) = 4.8 Hz, 1H, HHC(5) trans to HC(4)), 4.46 – 4.41 (m, 2H, H₂C(5′)), 4.40 (dd, 3J(H,H) = 9.7 Hz, 2J(H,H) = 9.3 Hz, 1H, HHC(5) cis to HC(4)), 4.24 (m, 1H, HC(4′)), 4.06 (′ddt′, 3J(H,H) = 7.0 Hz, 4J(H,H) = 2.2 Hz, 1H, HHC(11) syn), 3.94 (′dd′, 3J(H,H) = 7.0 Hz, 4J(H,H) = 2.2 Hz, 1H, HHC(9) syn), 3.18 (m, 3J(H,H) = 12.6 Hz, 1H, HHC(11) anti), 3.11 (m, 3J(H,H) = 12.2 Hz, 1H, HHC(9) anti), 2.13 (qqd, 3J(H,H) = 7.1, 6.8, 3.3 Hz, 1H, HC(6)), 2.03 (qqd, 3J(H,H) = 7.1, 6.8, 3.3 Hz, 1H, HC(6′)), 1.67 (s, 3H, C₆H₃), 1.61 (s, 3H, C₆H₃), 0.97 (d, 3J(H,H) = 7.1 Hz, 3H, H₃C(7)), 0.95 (d, 3J(H,H) = 7.1 Hz, 3H, H₃C(7′)), 0.95 (d, 3J(H,H) = 7.1 Hz, 3H, H₃C(7′)), 0.80 (d, 3J(H,H) = 6.8 Hz, 3H, H₃C(8')); 13C NMR (126 MHz, CD₂Cl₂, 295 K): δ = 173.2, 172.9 (C(2), C(2′)), 117.7 (C(10)), 74.4 (2C, C(4), C(4′)), 69.7, 69.6 (C(5), C(5′)), 62.7 (C(11)), 60.4 (C(9)), 41.1 (C₆), 30.7 (2C, C(6), C(6′)), 25.9 (2C, C₆H₃), 18.9, 18.8 (C(7), C(7′)), 14.2 (2C, C(8), C(8′)); IR: 2970, 2931, 2873, 1660, 1624, 1479, 1469, 1386, 1371, 1238, 1128, 1116, 958, 948, 827, 777, 758, 740; MS (ESI): m/z (%): 973 ([2M+PF₆]⁺, 49), 413 ([M⁺ – PF₆]⁺, 100); elemental analysis calcd (%) for C₁₈H₃₁N₂O₂F₆P₁Pd₁ (558.8): C 38.69, H 5.59, N 5.01; found: C 39.26, H 5.54, N 5.03.
Figure S1. Section of NOE spectrum for complex 12a recorded at 275 K.

12b. Ligand 6b (55.1 mg, 141 μmol) and [Pd(C₃H₅)Cl]₂ (25.8 mg, 70.5 μmol) were dissolved in CH₂Cl₂ (3 mL). The yellow solution was stirred for 3 hours at room temperature. Subsequently, a solution of AgPF₆ (39.4 mg, 156 μmol) in THF (4 mL) was added and stirring was continued for 10 minutes. The reaction mixture was finally filtered through a plug of Celite® and volatiles were evaporated. The crude product was obtained as a colorless solid (94 mg, 97%). A part of the product was dissolved in CH₂Cl₂ and the clear solution was washed with water. The organic phase was dried over Na₂SO₄ and volatiles were removed in vacuo. The product was isolated as an off-white solid.
\[^{1}H\] NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = 7.46\text{–}7.37 \) (m, 6H, arom CH), 7.34 (m, 2H, arom CH), 7.25 (m, 2H, arom CH), 5.78 (\('\text{dd}'\), \(^{3}\)J(H,H) = 12.6, 12.2, 7.0 Hz, 1H, HC(10)), 4.47 (\('\text{t}'\), \(^{2}\)J(H,H) = 9.3 Hz, \(^{3}\)J(H,H) = 9.3 Hz, 1H, HHHC(5(cis)) \text{ cis to HC(4) or to HC(4')}, 4.41 (\('\text{t}'\), \(^{2}\)J(H,H) = 9.2 Hz, \(^{3}\)J(H,H) = 9.2 Hz, 1H, HHHC(5(trans) \text{ trans to HC(4) or to HC(4')}, 4.39-4.33 (m, 1H, HC(4')), 4.29 (m, 2H, HC(5) \text{ trans to HC(4), HC(5') trans to HC(4')}), 4.26 (m, overlayed signal, 1H, HC(4)), 4.07 (\('\text{dd}'\), \(^{3}\)J(H,H) = 7.0 Hz, \(^{4}\)J(H,H) = 2.1 Hz, 1H, HC(11) \text{ syn }), 3.98 (\('\text{dd}'\), \(^{3}\)J(H,H) = 7.0 Hz, \(^{4}\)J(H,H) = 2.1 Hz, 1H, HC(9) \text{ syn }), 3.28 (\('\text{d}'\), \(^{3}\)J(H,H) = 12.6 Hz, 1H, HC(11)), 3.17 (\('\text{d}'\), \(^{3}\)J(H,H) = 12.2 Hz, 1H, HC(9)), 2.10 (\('\text{qqd}'\), \(^{3}\)J(H,H) = 7.1, 6.8, 6.9 Hz, 1H, HC(6)), 1.99 (\('\text{qqd}'\), \(^{3}\)J(H,H) = 7.1, 6.9, 3.0 Hz, 1H, HC(6')), 0.88 (d, \(^{3}\)J(H,H) = 7.1 Hz, 3H, H\text{C(7)}), 0.86 (d, \(^{3}\)J(H,H) = 7.1 Hz, 3H, H\text{C(7')}, 0.30 (d, \(^{3}\)J(H,H) = 6.8 Hz, 3H, H\text{C(8)})), 0.23 (d, \(^{3}\)J(H,H) = 6.9 Hz, 3H, H\text{C(8')}), \(^{13}\text{C}\) NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = 171.3, 170.9 \) (C(2), C(2')), 136.5, 136.5 (arom C \text{ ipso }), 129.9, 129.8 (arom CH \text{ para }), 118.3 (C(10)), 74.8 (2 C, C(4), C(4')), 69.5, 69.4 (C(5), C(5')), 63.2 (C(11)), 61.0 (C(9)), 59.9 (2 C, C(6), C(6')), 19.0, 18.9 (C(7), C(7')), 13.6, 13.5 (C(8), C(8')); IR: 3060, 2964, 2933, 2875, 1651, 1600, 1494, 1483, 1463, 1454, 1373, 1245, 1234, 1035, 947, 829, 746; MS (ESI): m/z (%): 537 ([M+−PF\textsubscript{6}], 100); elemental analysis calcd (%) for C\textsubscript{28}H\textsubscript{35}N\textsubscript{2}O\textsubscript{2}F\textsubscript{6}P\textsubscript{1}Pd\textsubscript{1} (683.0): C 49.24, H 5.17, N 4.10; found: C 48.94, H 5.35, N 4.03.

\textbf{15ax.} Same procedure as for \textbf{15ay}. The blue-green crystalline solid was dissolved in a minimum amount of CH\textsubscript{2}Cl\textsubscript{2} (0.5 mL) in a watch glass and kept aside on a shelf until crystals started to form. They were collected and subjected to single crystal analysis. IR: 2937, 2898, 2860, 1550, 1478, 1454, 1201, 1171, 1113, 1037, 1009, 984, 952, 941, 823, 794.

\textbf{15az.} Ligand (7az)-H (49 mg, 74 \textmu mol) was dissolved in methanol (3mL) and Cu(OAc)\textsubscript{2} (7.1 mg, 39 \textmu mol) was added in one portion. After 2 hours at room temperature, the volatiles were removed. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and the solution was washed with sat. aq. NaCl solution. The organic phase was separated and dried over Na\textsubscript{2}SO\textsubscript{4}. After removal of volatiles the remaining residue was dissolved in a minimum amount of Et\textsubscript{2}O and layered with pentane to yield turquoise needles that were subjected to X-ray diffraction analysis (19 mg, 37%). IR: 3027, 2966, 2933, 2877, 2857, 2823, 2804, 1566, 1482, 1453, 1360, 1274, 1190, 1155, 1118, 988, 954, 892, 840, 680; elemental analysis calcd (%) for C\textsubscript{56}H\textsubscript{52}B\textsubscript{2}CuF\textsubscript{24}N\textsubscript{4}O\textsubscript{4} (1386.2): C 48.52, H 3.78, N 4.04; found: C 50.72, H 4.28, N 3.76.

\textbf{15cx.} Same procedure as for \textbf{15ay}. The green crystalline solid was then dissolved in a minimum amount of CH\textsubscript{2}Cl\textsubscript{2} (0.5 mL) and layered with pentane. After 2 days, green cubes started to appear. They were collected and subjected to single crystal analysis. IR: 3031, 2925, 2898, 2853, 2825, 1571, 1546, 1535, 1496, 1454, 1366, 1206, 1170, 1048, 1036, 967, 940, 851, 698; MS (FAB) m/z (%): 842 ([M+H\textsuperscript{+}], 4), 812 ([M\textsuperscript{+}−Et]), 783 ([M\textsuperscript{+}−2Et]), 26), 453 ([M\textsuperscript{+}−7cx + H], 5).

\textbf{NMR-study of the syn-anti isomerization of complex 11cx (Figure S2).} Crystals of complex 11cx were finely ground and weighed (10.9 mg, 15.8 \textmu mol) into a NMR tube.
The NMR-tube and CDCl₃ were cooled in an ice bath and addition of CDCl₃ (0.7 mL) to the complex was carried out in a cold room (4°C). The tube was immediately vigorously shaken for about 10 seconds until the crystals were completely dissolved and placed in the spectrometer cooled to 275 K. The period of time between complete dissolution and the beginning of the first measurement was 5 minutes and 50 seconds. Measurements were recorded with an exponentially increasing number (2^x, maximum = 512) of dummy scans and 16 scans were used to record the ^1H NMR-spectrum. Time past was calculated by printed spectrometer time to which 5 minutes and 50 seconds were added and the time for 8 scans (8 x 4.18 seconds) was subtracted. The signals of the (anti, syn)-isomer were detectable after approx. 25 minutes. To calculate the isomeric ratio the following signals were integrated: ^1H NMR (500 MHz, CDCl₃, 275 K): δ((anti, syn)-isomer) = 6.62 (m, 2H, arom CH (D) ortho), 5.57 (d, ^3J(H,H) = 7.7 Hz, 1H, Ph(E)CH), 5.47 (dd, ^3J(H,H) = 11.5, 7.7 Hz, 1 H, (PhCH)₂CH), 4.48 (d, ^3J(H,H) = 11.5 Hz, 1H, Ph(F)CH); ((syn, syn)-isomer): 6.85 ('d', ^3J(H,H) = 6.9 Hz, 2H, arom CH (A) ortho), 5.82 (t, ^3J(H,H) = 11.1 Hz, 1H, (PhCH)₂CH). The ratio of isomers at room temperature ((syn, syn) to (anti, syn)) were determined in independent measurements as 91 : 9 in CD₂Cl₂ after 21 hours 20 min and 92 : 8 in CDCl₃ after 21 hours and 40 min of equilibration, respectively.

**Figure S2.** Increase of mole fraction of (syn, anti)-isomer over time in CDCl₃ at 275 K.

Allylic alkylation of rac-(E)-1,3-Diphenyl-2-propenyl-1-acetate with dimethyl malonate and BSA in the presence of a catalytic amount of complex 10az. rac-(E)-1,3-Diphenyl-2-propenyl-1-acetate (126 mg, 499 μmol) was added to a solution of complex 10az (8.1 mg, 10 μmol) in CH₂Cl₂ (1.65 mL), followed by dimethylmalonate (0.17 mL, 0.19 g, 1.5 mmol), BSA (0.37 mL, 0.30 g, 1.5 mmol) and a catalytic amount of KOAc. The mixture was degassed by 3 freeze/thaw-cycles and subsequently stirred at room temperature. The reaction was monitored by TLC (hexanes/EtOAc = 3:1). Even after 3 months neither the formation of product nor precipitation of palladium black was observed.

Stoichiometric reaction between complex 11cx and dimethyl malonate, BSA and tetrabutylammonium acetate. Under inert conditions a NMR sample of complex 11cx (11.6 mg, 16.8 μmol) in CD₂Cl₂ (0.8 mL) was prepared and BSA (7.3 μL, 51 μmol),
dimethyl malonate (3.8 μL, 33 μmol) and [Bu₄N]OAc (15.2 mg, 50.4 μmol) were added. 

$^1$H NMR spectra (500 MHz, 295 K) were repeatedly recorded over a period of 9 hours and 40 minutes. Neither complex decomposition nor product formation were observed.

**Ligand exchange experiments.** To a solution of 12b (9.5 mg, 14 μmol) in 0.52 mL of CD₂Cl₂ was added 1,3-bis(diphenylphosphino)propane (5.8 mg, 14 μmol) at room temperature. The yellow color intensified upon addition. $^1$H and $^{31}$P{$^1$H} experiments were recorded on a 500 MHz spectrometer at 295 K.

$^{31}$P{$^1$H} (125 MHz, CD₂Cl₂, 395 K): $\delta$ = 6.2; −145.4 (PF₆⁻) ppm.

To a solution of 10ay (7.5 mg, 14 μmol) in 0.52 mL of CD₂Cl₂ was added 1,3-bis(diphenylphosphino)propane (5.8 mg, 14 μmol) at room temperature. The colorless solution immediately turned yellow. $^1$H, $^{31}$P{$^1$H} and $^{11}$B experiments were recorded on a 500 MHz spectrometer at room temperature.

$^{31}$P{$^1$H} (125 MHz, CD₂Cl₂, 395 K): $\delta$ = 3.3 ppm.

**Note:** free 1,3-bis(diphenylphosphino)propane: $^{31}$P{$^1$H} (125 MHz, CD₂Cl₂, 395 K): $\delta$ = −18.0 ppm.
Calculations. All \textit{ab initio} calculations were carried out using the GAUSSIAN03 suite of programs at the DFT level with the LANL2DZ effective core potential for palladium while all other atoms were treated with explicit basis sets of 6-31G(d,p) quality.\footnote{[1]} Calculations started from a guess of the wave-function at the Hartree-Fock level and the wave function was improved until the level described was reached. To integrate the density functional the grid=ultrafine option was used. Then, structural optimizations followed that converged the total energy to better than $10^{-7}$ \(E_h\). To establish the validity of the approach chosen here, comparison with the experimental data from the crystal structure analyses described in this work were performed. The basis set and methods used here show good agreement with the structural parameters since deviations from experimental data were always in an acceptable range.

<table>
<thead>
<tr>
<th>Distances (in Å)</th>
<th>DFT</th>
<th>X-Ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N</td>
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<td>1.29</td>
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<tr>
<td>(C_{\text{oxa}}-X) (X = B, C)</td>
<td>1.52</td>
<td>1.52</td>
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<tr>
<td>N-Pd</td>
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<tr>
<td>Pd-C(_l)</td>
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<tr>
<td>Pd-C(_c)</td>
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<tr>
<td>Pd-C(_r)</td>
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<td>2.17</td>
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<table>
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<th>Angles (in°)</th>
<th>DFT</th>
<th>X-Ray</th>
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<tbody>
<tr>
<td>C(_r)-Pd-C(_r)</td>
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<td>N-Pd-N</td>
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<td>90.76</td>
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<tr>
<td>(C_{\text{oxa}}-X-C_{\text{oxa}}) (X = B, C)</td>
<td>114.59</td>
<td>111.19</td>
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</tbody>
</table>

\footnote{[a] Data were collected at 173K. [b] Bond lengths and angles for these compound were taken from reference [2] or calculated with ORTEP-3 (Version 1.08) from the fractional coordinates deposited in the CCDC. Data for these compounds were collected at 250K. [c] Data for this compound collected at 123K. [d] Allyl ligand was disordered.}


References
