

Supporting Information

Reactivity of an Oxoboryl Complex toward Fluorinated Aryl Boron Reagents

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I. General considerations

All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques unless noted otherwise. Hexane, toluene and dichloromethane were purified and dried using a M. Braun Solvent Purification System. Acetonitrile and deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles before use. Other solvent were distilled from appropriate drying agents.^[1] All solvents were stored under argon over activated molecular sieves. NMR spectra were acquired on a Bruker Avance 500 or a Bruker Avance 400 NMR spectrometer, respectively. Routine NMR measurements were performed on a Bruker Avance 200 NMR spectrometer. Chemical shifts (δ) are given in ppm. NMR spectra were referenced to external SiMe₄ via the residual protio solvent (¹H) or the solvent itself (¹³C), BF₃·OEt₂ (¹¹B), Cl₃CF (¹⁹F), MeNO₂ (¹⁵N) and 85% H₃PO₄ (³¹P), respectively. IR data of dichloromethane solutions or KBr pellets were acquired on a Bruker Vector 22 FT-IR spectrometer. IR spectra of pure materials, handled briefly under atmospheric conditions, were recorded on a Bruker ALPHA FT-IR apparatus equipped with a Platinum ATR module. Microanalyses were performed on an Elementar vario MICRO cube elemental analyzer. GC/MS experiments were performed on a Varian 320MS-GC/MS apparatus. The preparations of *trans*-[(Cy₃P)₂BrPt(B=O)] (**1**),^[2] and BPf₃ (Pf = C₆F₅)^[3] were performed following literature procedures. Ag[BAr^f₄] (Ar^f = C₆H₃-3,5-{CF₃}₂) was prepared analogously to Ag[BPf₄]^[4] from AgNO₃ and Na[BAr^f₄].^[5] All other compounds were purchased from commercial sources and degassed in vacuo.

II. Synthetic procedures and spectroscopic data

Preparation of *trans*-[(Cy₃P)₂(MeCN)Pt(B=O)][BAr^f₄] (3**).** A suspension of Ag[BAr^f₄] (91.5 mg, 94.2 μ mol) and acetonitrile (20.4 mg, 496.9 μ mol) in dichloromethane (0.3 mL) was added to a suspension of *trans*-[(Cy₃P)₂BrPt(B=O)] (**1**) (80.0 mg, 92.3 μ mol) in dichloromethane (0.3 mL) and the resulting mixture was vigorously shaken. After 2 h the brown precipitate was removed via filtration and washed twice with dichloromethane (0.4 mL). The combined filtrates were dried in vacuo yielding a yellow solid and addition of benzene (0.4 mL) caused formation of a biphasic liquid. The mixture was layered with hexane (0.2 mL) and after 15 h a crystalline solid had formed, which was isolated via decantation. Drying in vacuo gave spectroscopically pure *trans*-[(Cy₃P)₂(MeCN)Pt(B=O)][BAr^f₄] (**3**) as a pale yellow powder (64.3 mg, 41%). Single crystals suitable for X-ray diffraction studies were obtained from dichloromethane/ hexane via slow diffusion.

¹H NMR (500 MHz, CD₂Cl₂, 296.9 K): δ = 7.73 (m, 8H, *ortho*-H Ar^f), 7.57 (m, 4H, *para*-H Ar^f), 2.52 (s, 3H, MeCN), 2.46 (br m, 6H, Cy), 2.00–1.29 (m, 60H, Cy); ¹¹B{¹H} NMR (160 MHz, CD₂Cl₂, 295.9 K): δ = 12 (vbr s, FWHM = 2755 Hz, PtB=O), -7.55 (s, FWHM = 3 Hz, BAr^f₄); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 296.7 K): δ = 162.0

(q, $^1J_{B-C} = 50$ Hz, *ipso-C* Ar^f), 135.1 (br s, *ortho-C* Ar^f), 129.2 (qq, $^2J_{F-C} = 31$ Hz, $^3J_{B-C} = 3$ Hz, *meta-C* Ar^f), 126.1 (s, MeCN), 124.9 (q, $^1J_{F-C} = 272$ Hz, CF_3), 117.8 (sept, $^3J_{F-C} = 4$ Hz, *para-C* Ar^f), 35.8 (vt, $N = |^1J_{P-C} + ^3J_{P-C}| = 28$ Hz, C_1 Cy), 30.6 (s, $C_{3,5}$ Cy), 27.8 (vt, $N = |^2J_{P-C} + ^4J_{P-C}| = 11$ Hz, $C_{2,6}$ Cy), 26.4 (s, C_4 Cy), 4.0 (s, MeCN); ^{15}N HMBC (^{15}N : 51 MHz, 1H : 500 MHz, CD_2Cl_2 , 297.0 K): cross-peak between -191.8 (^{15}N) and 2.52 (1H); ^{19}F NMR (376 MHz, CD_2Cl_2 , 296.0 K): $\delta = -62.9$ (s); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2 , 297.2 K): $\delta = 35.9$ (s, $^1J_{Pt-P} = 2174$ Hz); IR (CH_2Cl_2 solution): 1885 (w, $^{10}B=O$), 1828 cm^{-1} (m, $^{11}B=O$); IR (pure): 1894 (m, $^{10}B=O$), 1836 cm^{-1} (s, $^{11}B=O$); Elemental analyses: calcd for $C_{70}H_{81}B_2F_{24}NOP_2Pt$: C 49.84, H 4.84, N 0.83; found: C 50.49, H 5.03, N 0.86.

Preparation of *trans*-[(Cy_3P) $_2$ BrPt($B=OBPF_3$)] (6). A suspension of BPf_3 (66.5 mg, 129.9 μ mol) and *trans*-[(Cy_3P) $_2$ BrPt($B=O$)] (1) (110.0 mg, 127.5 μ mol) in toluene (1 mL) was mixed thoroughly for one minute. The mixture became less turbid and was filtered. After 1 h at ambient temperature, microcrystalline needles had formed and the mixture was layered with hexane (1.5 mL) and stored at -30 °C. After 24 h the supernatant solution was decanted off and the colorless solid was dried in vacuo (142.0 mg, 81%). Single crystals suitable for X-ray diffraction studies were obtained by layering a benzene solution of **6** with hexane.

1H NMR (500 MHz, C_6D_6 , 296.8 K): $\delta = 2.72$ (br m, 6H, Cy), 1.91–1.01 (m, 60H, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6 , 296.4 K): $\delta = 22$ (vbr s, FWHM = 3369 Hz, Pt $B=O$), -2 (br s, FWHM = 1050 Hz, $OBPF_3$); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6 , 296.7 K): $\delta = 148.8$ (br d, $^1J_{F-C} = 246$ Hz, Pf), 140.7 (br d, $^1J_{F-C} = 253$ Hz, Pf), 137.6 (br d, $^1J_{F-C} = 261$ Hz, Pf), 119.2 (br s, Pf), 36.2 (br s, C_1 Cy), 30.7 (s, $C_{3,5}$ Cy), 27.2 (vt, $N = |^2J_{P-C} + ^4J_{P-C}| = 11$ Hz, $C_{2,6}$ Cy), 26.4 (s, C_4 Cy); ^{19}F NMR (376 MHz, C_6D_6 , 296.0 K): $\delta = -132.2$ (m, 6F), -156.8 (m, 3F), -163.4 (m, 6F); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6 , 297.2 K): $\delta = 33.7$ (s, $^1J_{Pt-P} = 2065$ Hz); IR (CH_2Cl_2 solution): 1773 (w, $^{10}B=O$), 1721 cm^{-1} (m, $^{11}B=O$); IR (pure): 1769 (m, $^{10}B=O$), 1714 cm^{-1} (s, $^{11}B=O$); Elemental analyses: calcd for $C_{54}H_{66}B_2BrF_{15}OP_2Pt$: C 47.18, H 4.84; found: C 47.32, H 4.92.

III. Crystallographic structure determination

The crystal data were collected on a Bruker X8 Apex II diffractometer with a CCD area detector and multi-layer mirror monochromated MoK_{α} radiation. The structures were solved using direct methods, refined with the Shelx software package^[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to idealized positions and were included in structure factors calculations. Crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, under reference nos. CCDC 777642 (**3**), 777643 (**5**) and 777644 (**6**), respectively.

Crystal data for *trans*-[(Cy₃P)₂(MeCN)Pt(B≡O)][BAR^f₄] (3) · 0.5CH₂Cl₂. C_{70.50}H₈₂B₂ClF₂₄NOP₂Pt, *M_r* = 1729.47, colorless block, 0.34×0.31×0.22 mm³, triclinic space group *P* $\bar{1}$, *a* = 13.2444(10) Å, *b* = 17.0408(14) Å, *c* = 19.2096(17) Å, α = 113.808(3)°, β = 90.612(3)°, γ = 109.200(3)°, *V* = 3694.0(5) Å³, *Z* = 2, ρ_{calcd} = 1.555 g cm⁻³, μ = 2.082 mm⁻¹, *F*(000) = 1742, *T* = 100(2) K, *R_I* = 0.0430, *wR*² = 0.0892, 15421 independent reflections [$2\theta \leq 53.58^\circ$] and 957 parameters.

Crystal data for *trans*-[(Cy₃P)₂BrPt(B≡O)BAR^f₃] (5). C₆₀H₇₅B₂BrF₁₈OP₂Pt, *M_r* = 1512.76, colorless block, 0.32×0.21×0.17 mm³, triclinic space group *P* $\bar{1}$, *a* = 13.507(4) Å, *b* = 13.589(4) Å, *c* = 18.517(6) Å, α = 84.383(14)°, β = 88.103(13)°, γ = 80.059(12)°, *V* = 3331.3(17) Å³, *Z* = 2, ρ_{calcd} = 1.508 g cm⁻³, μ = 2.842 mm⁻¹, *F*(000) = 1516, *T* = 100(2) K, *R_I* = 0.0292, *wR*² = 0.0608, 14106 independent reflections [$2\theta \leq 53.58^\circ$] and 776 parameters.

Crystal data for *trans*-[(Cy₃P)₂BrPt(B≡O)BPf₃] (6) · C₆H₆ · 0.5C₆H₁₄. C₆₃H₇₉B₂BrF₁₅OP₂Pt, *M_r* = 1495.82, colorless needle, 0.20×0.08×0.02 mm³, triclinic space group *P* $\bar{1}$, *a* = 10.222(2) Å, *b* = 14.849(3) Å, *c* = 22.181(6) Å, α = 106.704(16)°, β = 96.707(17)°, γ = 104.199(11)°, *V* = 3061.7(13) Å³, *Z* = 2, ρ_{calcd} = 1.623 g cm⁻³, μ = 3.084 mm⁻¹, *F*(000) = 1506, *T* = 100(2) K, *R_I* = 0.0774, *wR*² = 0.1539, 12662 independent reflections [$2\theta \leq 53.6^\circ$] and 725 parameters.

IV. References

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