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Boron Ligands

Synthesis and Structure of a Cationic Platinum Borylene Complex**

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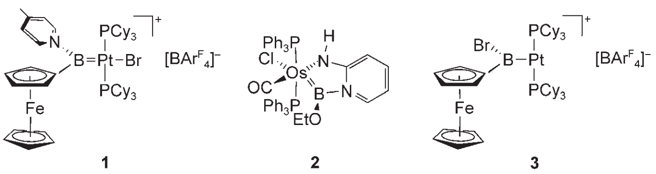
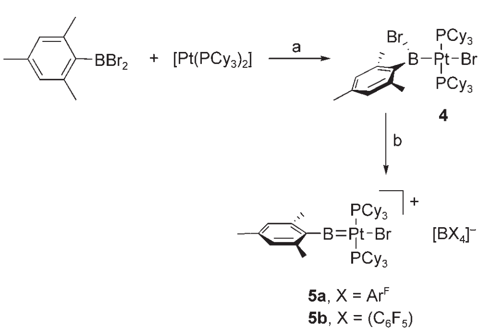
Terminal borylene complexes with two-coordinate boron atoms were first reported in 1998[1] and have since attracted significant interest owing to their close relationship to ubiquitous carbonyl complexes[2] and, moreover, because of their propensity to serve as unique sources for elusive borylene units (B–R) under ambient conditions. The latter has allowed for the versatile and synthetically very useful borylene transfer to various transition-metal fragments[3] or even to unsaturated organic substrates.[4] To date, the range of neutral terminal borylene complexes is limited to the early transition metals V,[3b] Cr,[3a,5] and W.[1] Furthermore, a few cationic species have been reported exclusively for Fe.[4b,6] Corresponding terminal borylene complexes of the late transition metals, however, have not been realized as of yet, with the exception of the base-stabilized platinum species **1** (Scheme 1). Although this compound can be considered in a very formal sense as the 4-methylpyridine adduct of a borylene complex, the boron center displays predominantly boryl character owing to its increased coordination number.[7] A very similar finding was made for the base-stabilized compound **2** and related osmium complexes, which display Os–B bond lengths more characteristic for osmium boryl complexes [L_xOs–BR$_2$].[8]



Scheme 1. Molecular structure of the base-stabilized borylene complexes **1** and **2** and the T-shaped boryl complex **3**, the precursor of **1**; Cy = cyclohexyl, Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$.

While complexes with significant Pt–B multiple-bond character have so far remained unknown, the chemistry of platinum–boron compounds is otherwise very well-established. In particular, platinum boryl complexes of the type [L_xPt–BR$_2$] are numerous and thoroughly investigated,[9] mostly owing to their importance as key intermediates for the metal-mediated diboration of organic substrates.[10] Moreover, Pt and to a somewhat lesser extent Pd have proven to form transition-metal complexes with boron-centered ligands in far more unusual coordination modes, including metal base-stabilized boryl[11] and borylene species[3c,12] or heterodinuclear borylene complexes.[13] Herein we report on the first platinum borylene species with a two-coordinate boron center and pronounced Pt–B-multiple-bond character.

Recently, we described the formation of *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Fc)Br}] (Fc = ferrocenyl) upon oxidative addition of [FcBBr$_2$] to [Pt(PCy$_3$)$_2$],[14] and its conversion to the unprecedented T-shaped three-coordinate platinum boryl complex *trans*-[(Cy$_3$P)$_2$Pt{B(Fc)Br}][BAr$^F_4$] (**3**), which was obtained by selective bromide abstraction from the Pt center. Subsequently, **3** was converted to **1** by addition of 4-methylpyridine to the boron atom with concomitant formal migration of bromide from the B to Pt atom.[7] Similarly, we have now obtained the boryl complex *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Mes)Br}] (**4**) by mixing equimolar amounts of [Pt(PCy$_3$)$_2$] and MesBBr$_2$ in benzene (Scheme 2). Instantaneously, a white solid is formed and the precipitation of the product is completed upon addition of hexane. Multinuclear NMR data of the isolated solid (88% yield) are consistent with the formulation of **4**. The $^{11}\text{B}\{^{1}\text{H}\}$ NMR spectrum features a broad signal at $\delta = 68.7$ ppm, which is slightly downfield-shifted with respect to that of the starting borane ($\delta = 61.7$ ppm).[15] In the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum a singlet at $\delta = 18.9$ ppm ($^{1}J_{\text{P-Pt}} = 3054$ Hz) is observed, which is strongly upfield-shifted in comparison to that of [Pt(PCy$_3$)$_2$] ($\delta = 61.9$ ppm, $^{1}J_{\text{P-Pt}} = 4120$ Hz).[16] The presence of the mesitylbromoboryl group is confirmed by the ^{1}H NMR spectrum, which shows a broad resonance for the aryl protons at $\delta = 6.83$ ppm in CD$_2$Cl$_2$ (two respective signals are found in benzene), two for the methyl groups in *ortho* position at $\delta = 3.61$ and 2.79 ppm, and one sharp signal for the methyl substituent in *para* position at $\delta = 2.18$ ppm. The presence of two chemically nonequivalent *ortho*-methyl groups indicates



Scheme 2. Synthesis of **4** and **5a b**. a) C$_6$H$_6$; b) Na[BAr$^F_4$] or K[B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$.

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hindered rotation around the $B{-}C_{ipso}$ bond, which is further substantiated by variable-temperature ^{1}H NMR spectroscopy in deuterated toluene. At −10 °C the corresponding signals are sharper ($\delta = 6.89$ and 6.78 ppm for the two aryl protons, $\delta = 4.00$ and 3.05 ppm for the *ortho*-methyl groups), while heating to 100 °C leads to coalescence of the two nonequivalent aryl proton resonances ($\delta = 6.81$ ppm) and methyl groups ($\delta = 3.38$ ppm), respectively.

A single crystal suitable for an X-ray diffraction study could be obtained from a solution of **4** in benzene by slow evaporation of the solvent. The molecular structure and relevant bond lengths and angles are displayed in Figure 1.[17]

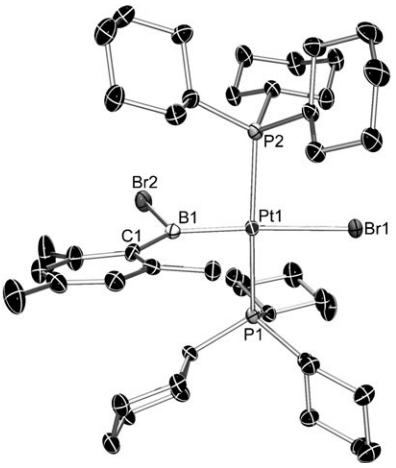

Figure 1. Molecular structure of **4**; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1-B1 2.009(4), Pt1-Br1 2.6246(4), B1-Br2 2.006(4), B1-C1 1.587(5); Pt1-B1-C1 132.2(3).

The Pt−Br bond length (2.6246(4) Å) is comparable to that of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (2.6183(8) Å), but longer than that in *trans*-$[(Cy_3P)_2PtBr_2]$ (2.435(1) Å).[18] The Pt−B bond length (Pt1−B1 2.009(4) Å) is very similar to that in *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (1.9963(34) Å)[14] or *trans*-$[(Ph_3P)_2Pt(Cl)(BCat)]$ (2.008(8) Å; Cat = catecholato).[19] The boryl group is oriented orthogonally to the $\{PtP_2\}$ fragment (C1-B1-Pt1-P1 90.6(4)°). Compound **4** is very air- and moisture-sensitive, and shows slow decomposition in solution, but can be stored as a solid under argon.

Treatment of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Mes)Br\}]$ with $Na[BAr^F{}_4]$ in CD_2Cl_2 afforded precipitation of a white powder (NaBr). The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture shows a new singlet at $\delta = 45.0$ ppm ($^1J_{P\text{-}Pt} = 2072$ Hz), strongly downfield-shifted with respect to the corresponding boryl complex. The ^{1}H NMR spectra features only one sharp signal for the two aryl protons ($\delta = 7.01$ ppm) and the *ortho*-methyl groups ($\delta = 2.72$ ppm) of the mesityl fragment ($\delta = 2.34$ ppm for the *para*-methyl group). In the $^{11}B\{^1H\}$ NMR spectra only the resonance for the $[BAr^F{}_4]^-$ ion can be detected at $\delta = -7.55$ ppm, probably owing to unresolved coupling to the platinum and phosphorus nuclei.[20]

Attempts to grow suitable crystals for X-ray diffraction analysis failed, and thus, we repeated the reaction with $K[B(C_6F_5)_4]$ as the halide-abstraction reagent. Multinuclear NMR data show the same set of signals in the $^{31}P\{^1H\}$ NMR and ^{1}H NMR spectra, while the $^{11}B\{^1H\}$ NMR spectrum displays a singlet at $\delta = -17.62$ ppm for the $[B(C_6F_5)_4]^-$ ion. A single crystal, isolated by layering the reaction mixture with hexane and cooling to −35 °C, could be analyzed by X-ray diffraction, proving the constitution of the product as the first terminal platinum borylene complex *trans*-$[(Cy_3P)_2Pt(Br)(BMes)][B(C_6F_5)_4]$ (**5b**; see Scheme 2).[17]

The complex crystallizes in the space group $P2_1/n$. The boron atom is two-coordinate and linearly bound to its neighboring atoms Pt and C (Pt1-B1-C1 178.15(9)°; Figure 2).

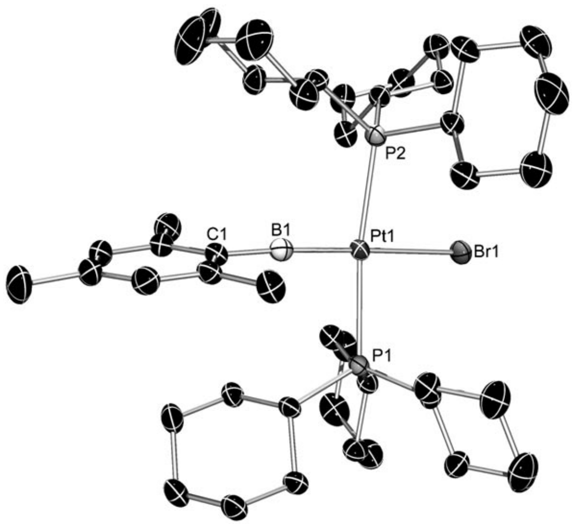

Figure 2. Molecular structure of **5b**; thermal ellipsoids are set at 50% probability. Hydrogen atoms as well as the $[B(C_6F_5)_4]^-$ ion and cocrystallized CH_2Cl_2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1-B1 1.859(3), Pt1-Br1 2.5418(6), B1-C1 1.495(4); Pt1-B1-C1 178.15(9).

The Pt−B bond (1.859(3) Å) is significantly shorter when compared to the boryl complex **4** (2.009(4) Å), and to the base-stabilized species **1** (2.014(5) Å)[7] or $[(\eta^5\text{-}C_5Me_5)(CO)Fe(\mu\text{-}CO)Pt(PCy_3)(\mu\text{-}Br)Pt(PCy_3)Br(\mu^3\text{-}B)]$ (B−Pt2 1.938(4) Å; B−Pt1 2.158(4) Å),[3c] which all display three-coordinate boron centers. This bond is also about 10 pm shorter than that in the iminoboryl complex *trans*-$[(Cy_3P)_2(Br)Pt{-}B{\equiv}N{-}SiMe_3]$ (1.960(3) Å), which shows an unusual boron atom that is only two-coordinate, however electronically saturated by an effective BN triple bond, and hence, of boryl character.[21] These findings are consistent with the significant multiple-bond character of the B−Pt linkage in *trans*-$[(Cy_3P)_2Pt(Br)(BMes)]^+$. Further electronic stabilization of the coordinatively unsaturated boron atom in **5** could be provided by interaction with the mesityl group as indicated by a $B{-}C_{ipso}$ bond (1.495(4) Å) that is significantly shorter than that in the boryl complex **4** (1.587(5) Å). A similar observation was made for a related cationic iron borylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+$ ($B{-}C_{ipso}$ 1.491(10) Å), in comparison with its boryl precursor $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2\{B(Br)Mes\}]$ ($B{-}C_{ipso}$ 1.569(3) Å).[6a] The

Pt–Br bond length (2.5418(6) Å) in **5b** is comparable to the one in *trans*-[$(Cy_3P)_2(Br)Pt{-}B{\equiv}N{-}SiMe_3$] (2.5516(4) Å),[21] but shorter with respect to the boryl complex **4** (2.6246(4) Å), thus indicating a weaker *trans* influence of the borylene and iminoboryl ligands, respectively.[22]

To gain deeper insight in the bonding situation of **5**, Kohn–Sham orbitals were examined,[23] resulting in two orbitals with considerable Pt–B σ-bonding character. Figure 3 shows the p_z orbital of the boron atom and the ($d_{z^2} + d_{x^2-y^2}$) hybrid of the platinum atom. Additionally, two orbitals (HOMO−8 and HOMO−16) were identified, which characterize both orthogonal π components of the Pt–B bond. These molecular orbitals consist of B(p_x) and Pt(d_{xz}) as well as B(p_y) and Pt(d_{yz}) atomic orbitals, respectively.

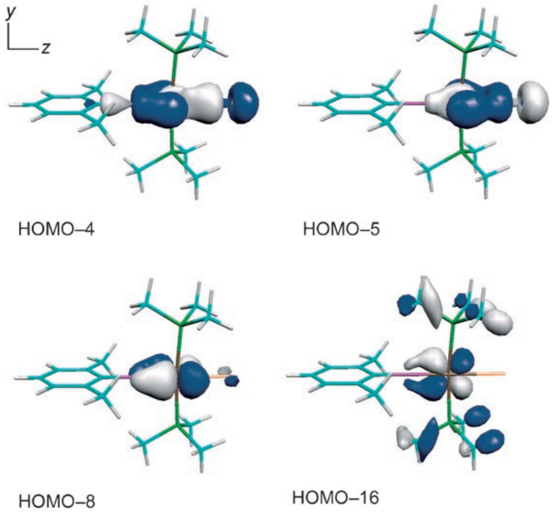

Figure 3. Kohn–Sham orbitals of σ and π components of the Pt–B bond in *trans*-[$(Me_3P)_2Pt(Br)(BXyl)$]$^+$ (Xyl = xylyl); H white, Br orange, B pink, C blue, P green, Pt brown.

In contrast to [$(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)$]$^+$ neither the p_y orbital of the boron atom nor the d_{yz} orbital of the platinum atom plays a pronounced role in the in-phase π-type interaction with the aromatic ring.[6a] Hence, the short B–C_{ipso} distance of **5b** when compared to that of **4** could merely be an effect of the decreased coordination number and the positive charge at the boron center.

Computations on the cationic mesityl-, *ortho*,*ortho*-xylyl-, *ortho*-tolyl-, and phenyl-substituted platinum arylborylene and T-shaped aryl(bromo)boryl analogues of **3** revealed that only the former two cations are thermodynamically more stable in their borylene form (13.9 and 10.3 kJ mol^{-1}), thus suggesting that for the stability of **5**, both steric and electronic effects are responsible.

In summary, the first base-free platinum borylene complex was obtained from a *trans*-bromoboryl(bromo)platinum precursor. Interestingly, its formation occurred by selective bromide abstraction from the boron atom, thus in sharp contrast to the earlier observed synthesis of cationic platinum boryl complexes by bromide abstraction from the metal center. Computations underline the decisive role of the boron-bound substituent in these interesting transformations.

Experimental Section

4: Br_2BMes (0.038 g, 0.132 mmol) was dissolved in C_6H_6 (1.0 mL) and added to solid [$Pt(PCy_3)_2$] (0.100 g, 0.132 mmol). The pale yellow solution was layered with hexane (1.0 mL) and immediately a white solid precipitated. The solid was allowed to settle and was separated and washed with hexanes. After drying, 122 mg of **4** was isolated (88 %). Crystals suitable for an X-ray diffraction study were obtained by recrystallization from a mixture of C_6H_6 and hexane by slow evaporation of the solvent. ^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): $\delta =$ 6.83 (2 overlapping br s, 2 H, CH), 3.61 (br s, 3 H, *o*-CH_3, Mes), 2.79 (br s, 3 H, *o*-CH_3, Mes), 2.30–2.05 (m, 6 H, Cy), 2.18 (s, 3 H, *p*-CH_3, Mes), 1.90–1.55 (m, 36 H, Cy), 1.25–1.00 ppm (m, 18 H, Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): $\delta = 140.7$ (s, *o*-C, Mes, from 2D-HMBC), 131.5 (s, *m*-C, Mes, from 2D-HMQC), 130.7 (s, *o*-C, Mes, from 2D-HMBC), 129.8 (s, *m*-C, Mes, from 2D-HMQC), 128.2 (s, *i*-C, Mes, from 2D-HMQC), 35.7 (vt, C^1, Cy, $N = 26$ Hz), 31.0–29.8 (3 overlapping s, 2 *o*-CH_3, Mes and $C^{3,5}$, Cy, from 2D-HMQC), 27.8 (br s, $C^{2,6}$, Cy), 26.8 (s, C^4, Cy), 21.0 ppm (s, *p*-CH_3, Mes) (because of the poor solubility of the compound not all signals of the Mes group could be detected); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta =$ 68.7 ppm (br s); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta =$ 18.9 ppm (s, $^1J_{P\text{-}Pt} = 3054$ Hz). Elemental analysis (%) calcd for $C_{45}H_{77}BBr_2P_2Pt{\cdot}C_6H_6$: C 54.50, H 7.44; found: C 54.38, H 7.07.

5a: Compound **4** (0.024 g, 0.023 mmol) and Na[$BAr^F{}_4$] (0.020 g, 0.023 mmol) were put in a J. Young NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture turned slightly yellow after 5 min, and some fine powder precipitate (NaBr) was observed. Multinuclear NMR spectra showed complete conversion of the starting material and formation of **5a**. After filtering over glass-fiber filter paper the solution was layered with hexane (1.0 mL) and stored at −35 °C. After one week pale yellow crystals precipitated (0.030 g, 71 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 21 °C): $\delta = 7.73$ (m, 8 H, *o*-CH, $BAr^F{}_4$), 7.57 (br s, 4 H, *p*-CH, $BAr^F{}_4$), 7.01 (m, 2 H, CH, Mes), 2.75 (m, 6 H, Cy), 2.72 (s, 6 H, *o*-CH_3, Mes), 2.34 (s, 3 H, *p*-CH_3, Mes), 2.06–1.99 (m, 12 H, Cy), 1.79–1.60 (m, 30 H, Cy), 1.12–1.00 ppm (m, 18 H, Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 21 °C): $\delta = 162.0$ (q, *i*-C, $BAr^F{}_4$, $^1J_{C\text{-}B} = 50$ Hz), 150.9 (s, *p*-C, Mes), 146.9 (s, *o*-C, Mes), 135.1 (s, *o*-C, $BAr^F{}_4$), 130.0 (s, *m*-C, Mes), 129.2 (q, *m*-C, $BAr^F{}_4$, $^2J_{C\text{-}F} = 31$ Hz), 124.9 (q, CF_3, $BAr^F{}_4$, $^1J_{C\text{-}F} = 272$ Hz), 117.7 (sep, *p*-C, $BAr^F{}_4$, $^3J_{C\text{-}F} = 4$ Hz), 37.4 (vt, C^1, Cy, $N = 29$ Hz), 30.4 (s, $C^{3,5}$, Cy), 27.3 (vt, $C^{2,6}$, Cy, $N =$ 12 Hz), 26.0 (s, C^4, Cy), 23.1 (s, *o*-CH_3, Mes), 22.4 ppm (s, *p*-CH_3, Mes); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 21 °C): $\delta = -7.6$ ppm (s, $BAr^F{}_4$); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 21 °C): $\delta = 45.0$ ppm (s, $^1J_{P\text{-}Pt} = 2072$ Hz). Elemental analyses (%) calcd for $C_{77}H_{89}B_2BrF_{24}P_2Pt$: C 50.56, H 4.90; found: C 50.81, H 4.85.

5b: Compound **4** (0.035 g, 0.033 mmol) and K[$B(C_6F_5)_4$] (0.024 g, 0.033 mmol) were put in a J. Young NMR tube and dissolved in CD_2Cl_2 (0.6 mL). The reaction mixture turned slightly yellow after 5 min, and some fine powder precipitate (KBr) was observed. Multinuclear NMR spectra showed complete conversion of the starting material and formation of **5b**. After filtering over glass-fiber filter paper the solution was layered with hexane (1.0 mL) and stored at −35 °C. After one week pale yellow crystals precipitated (0.035 g, 64 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): $\delta = 7.02$ (m, 2 H, CH, Mes), 2.76 (m, 6 H, Cy), 2.72 (s, 6 H, *o*-CH_3, Mes), 2.36 (s, 3 H, *p*-CH_3, Mes), 2.06–1.99 (m, 12 H, Cy), 1.79–1.60 (m, 30 H, Cy), 1.12–1.00 ppm (m, 18 H, Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 22 °C): $\delta = 150.9$ (s, *p*-C, Mes), 148.4 (d, *p*-C, [$B(C_6F_5)_4$], $^1J_{C\text{-}F} = 244$ Hz), 146.9 (s, *o*-C, Mes), 138.5 (d, *o*/*m*-C, [$B(C_6F_5)_4$], $^1J_{C\text{-}F} = 244$ Hz), 136.6 (d, *o*/*m*-C, [$B(C_6F_5)_4$], $^1J_{C\text{-}F} = 244$ Hz), 130.0 (s, *m*-C, Mes), 124.9 (br s, *i*-C, [$B(C_6F_5)_4$]), 37.4 (vt, C^1, Cy, $N = 29$ Hz), 30.4 (s, $C^{3,5}$, Cy), 27.3 (vt, $C^{2,6}$, Cy, $N = 12$ Hz), 26.0 (s, C^4, Cy), 23.0 (s, *o*-CH_3, Mes), 22.5 ppm (s, *p*-CH_3, Mes); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 22 °C): $\delta = -17.6$ ppm (s, [$B(C_6F_5)_4$]); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 22 °C): $\delta = 45.0$ ppm (s, $^1J_{\text{P-Pt}} = 2073$ Hz). Elemental analyses (%) calcd for $C_{69}H_{77}B_2BrF_{20}P_2Pt{\cdot}CH_2Cl_2$: C 48.60, H 4.60; found: C 48.54, H 4.68.

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[17] The crystal data of **4** and **5b** were collected on a Bruker APEX diffractometer with CCD area detector and graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved by using direct methods, refined with the SHELX software package (G. Sheldrick, University of Göttingen, **1997**) and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations. Crystal data for **4**: $C_{51}H_{83}BBr_2P_2Pt$, $M_r = 1123.83$, colorless block, $0.20 \times 0.17 \times 0.07$ mm^3, monoclinic, space group $P2_1/c$, $a = 13.1450(8)$, $b = 23.0520(15)$, $c = 16.9923(11)$ Å, $\beta = 105.2100(10)°$, $V = 4968.6(5)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.502$ g cm^{-3}, $\mu = 4.530$ mm^{-1}, $F(000) = 2288$, $T = 173(2)$ K, $R_1 = 0.0399$, $wR^2 = 0.0712$, 9856 independent reflections [$2\theta = 52.28°$] and 517 parameters. Crystal data for **5b**: $C_{70}H_{79}B_2BrCl_2F_{20}P_2Pt$, $M_r = 1729.79$, colourless block, $0.33 \times 0.31 \times 0.22$ mm^3, monoclinic, space group $P2_1/n$, $a = 16.160(5)$, $b = 24.965(7)$, $c = 18.780(5)$ Å, $\beta = 110.240(12)°$, $V = 7109(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.616$ g cm^{-3}, $\mu = 2.750$ mm^{-1}, $F(000) = 3464$, $T = 173(2)$ K, $R_1 = 0.0317$, $wR^2 = 0.0623$, 14109 independent reflections [$2\theta = 52.48°$] and 886 parameters. CCCDC-631652 and CCDC-631653 contain 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.

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