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T-Shaped Platinum Boryl Complexes: Synthesis and Structure

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Abstract: A series of cationic T-shaped 14-electron boryl complexes of the type *trans*-$[(Cy_3P)_2Pt\{B(X)X'\}]^+$ (X = Br; X′ = *ortho*-tolyl, *t*Bu, NMe_2, piperidyl, Br; XX′ = $(NMe_2)_2$, catecholato) were synthesized by halide abstraction from *trans*-$[(Cy_3P)_2Pt(Br)\{B(X)X'\}]$ (Cy = cyclohexyl) with $Na[BAr^f_4]$ (Ar^f = 3,5-$(CF_3)_2C_6H_3$), $K[B(C_6F_5)_4]$, or $Na[BPh_4]$. X-ray diffraction studies were performed on all compounds, revealing a subtle correlation between the *trans*-influence of the boryl moiety and the Pt–H and Pt–C separations. However, no notable agostic C–H interaction with the platinum center was detected. *trans*-$[(Cy_3P)_2Pt(BCat)]^+$ (Cat = catecholato), the complex with the shortest Pt–H and Pt–C distances, was treated with Lewis bases (L), forming compounds of the type *trans*-$[(Cy_3P)_2Pt(L)(BCat)]^+$, thus proving a decisive influence of the degree of *trans*-influence exerted by the boryl ligands on the chemical reactivity of the title complexes. Another point that was investigated and clarified is the different behavior of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Mes\}]$ (Mes = mesityl) towards $K[B(C_6F_5)_4]$ with formation of the borylene species *trans*-$[(Cy_3P)_2Pt(Br)(BMes)]^+$.

Keywords: boryl complexes · platinum · synthetic methods · *trans*-influence · T-shaped geometry

Introduction

Transition-metal boryl complexes[1] are of significant interest because they are key intermediates in catalytic processes such as hydroboration,[2] diboration,[3] and C–H activation of organic substrates.[4] Corresponding platinum species $[L_xPt–BR_2]$, which are most relevant to the boryl-based functionalization of alkynes, olefins, and diazo compounds,[5] are commonly prepared by oxidative addition of B–E (E = main group element) bonds to low-valent Pt species.[1] Haloboranes $R_2B–Hal$ (Hal = Cl, Br, I) turned out to be valuable starting materials, and a range of boryl complexes have been isolated in the recent years.[6] The most remarkable feature of these complexes is the strong *trans*-influence of the boryl moiety, which was investigated by means of computational[7] and experimental studies.[6e] In particular, boryl complexes *trans*-$[(Cy_3P)_2Pt(Br)\{B(X)X'\}]$ (Cy = cyclohexyl = C_6H_{11}) have been investigated with respect to the degree of *trans*-influence imposed by the different boryls, giving the following scale: –BCat-4-*t*Bu < $-BBr_2$ < –B(Br)*o*Tol < –B(Br)NMe_2 < –B(Br)Fc < –B(Br)Mes < $-B(NMe_2)_2$ < –B(Br)Pip < –B(Br)*t*Bu (Cat = catecholato = 1,2-O_2-C_6H_4, *o*Tol = *ortho*-tolyl = 2-CH_3-C_6H_4, Fc = ferrocenyl = (η^5-C_5H_4)Fe(η^5-C_5H_5), Mes = mesityl = 2,6-$(CH_3)_2$-C_6H_3, Pip = piperidyl = NC_5H_{10}).[6e] Given the success in preparing complexes by oxidative addition of bromoboranes,[6c–i,8] and the strong *trans*-influence of the boryl moiety, it was possible to prepare and structurally characterize the unusual 14-electron T-shaped Pt boryl complex *trans*-$[(Cy_3P)_2Pt\{B(Br)Fc\}]^+$ (**1**)[9] upon addition of $Na[BAr^f_4]$ (Ar^f = 3,5-$(CF_3)_2C_6H_3$) to the boryl complex *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Fc\}]$ (**2**).[6g] Remarkably, complex **1** is devoid of any agostic interaction or solvent coordination at the vacant site, thus displaying an electronically and coordinatively unsaturated Pt^{II} center.

Such 14-electron platinum(II) compounds are very important owing to their central role in alkane C–H activation,[10] or as models for intermediates in the olefin polymerization catalyzed by late transition metals.[11] Of this kind of Pt species only a handful have been reported, as they are often transient or contain coordinated solvent molecules. Presumably, bulky ligands are necessary to protect the free coordination site to isolate stable 14-electron T-shaped Pt^{II} compounds. The group of Spencer has reported a number of β-agostic C–H-stabilized complexes of the type $[Pt(R)(PP)]^+$ (PP = chelating bisphosphine; R = alkyl).[11b,12] Ingelson and co-workers described the cationic compound $[Pt(CH_3)(P\mathit{i}Pr_3)_2]^+$, which is stabilized by a β-agostic C–H bond,[13]

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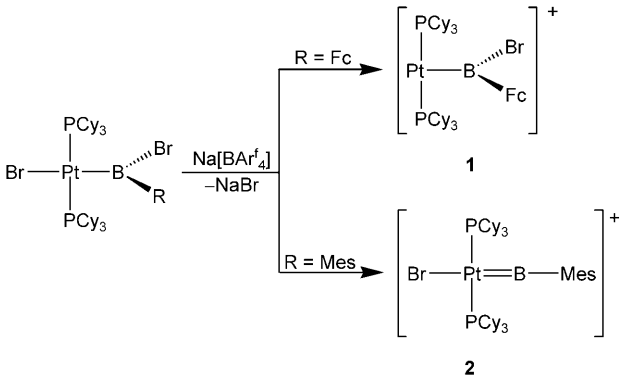
whereas Barrata et al. prepared the complexes $[Pt(CH_3)\{PR_2(2,6\text{-}Me_2C_6H_3)\}_2]^+$ (R = Ph, Cy), which are supported by a δ-agostic C–H interaction.[14]

In sharp contrast to the aforementioned reactivity of **2** towards $Na[BAr^f_4]$, the corresponding bromide abstraction from *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Mes\}]$ (**3**) under identical conditions did not yield a T-shaped Pt boryl species, but *trans*-$[(Cy_3P)_2Pt(Br)(BMes)]^+$ (**4**), and thus, the first example of a platinum borylene complex without base stablilization.[6f] The outcome of the latter reaction might imply that both sites—that is, Pt–Br and B–Br—are susceptible to bromide abstraction with formation of different products (Scheme 1). It should be mentioned that the elimination of Br^- from bromoboryl complexes $[(\eta^5\text{-}C_5R_5(OC)_2Fe\text{–}B(R)Br]$ was previously utilized by Aldridge for the synthesis of the first cationic borylene complexes $[(\eta^5\text{-}C_5R_5(OC)_2Fe{=}BR]\ [BAr^f_4]$.[15]

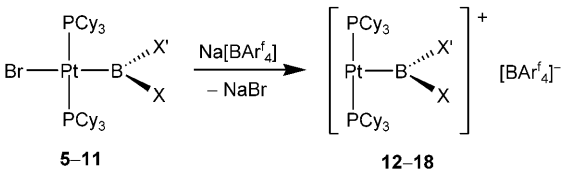


Scheme 1. Two different types of products, T-shaped Pt boryl complex **1** and borylene species **4**, isolated from similar reactions, that is, *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)X\}]$ (X = Fc, Mes) and $Na[BAr^f_4]$.

To gain further insight into the different behavior of the platinum boryl complexes *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)X\}]$ (X = Fc, Mes)[6f,g] toward halide abstraction, a range of related complexes of the type *trans*-$[(Cy_3P)_2Pt(Br)\{B(X)X'\}]$ (X = Br, X′ = *o*Tol, *t*Bu, NMe_2, Pip, Br; XX′ = $(NMe_2)_2$, Cat)[6e] (**5**–**11**) were treated with $Na[BAr^f_4]$, $K[B(C_6F_5)_4]$, or $Na[BPh_4]$ in dichloromethane. Herein we report for the first time the full characterization of a series of 14-electron T-shaped platinum boryl complexes, thus allowing a detailed investigation of the subtle influence that different boryl ligands exert on the degree of C–H agostic interactions, and consequently on the reactivity of these species. Low-temperature NMR spectra of *trans*-$[(Cy_3P)_2Pt(BCat)]^+$ were recorded, and its reactivity towards Lewis bases was investigated. Furthermore, the exceptional behavior of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Mes\}]$ (**3**) towards bromide abstraction was clarified.

Table 1. $^{31}P\{^1H\}$ NMR spectroscopy data of the cationic boryl complexes *trans*-$[(Cy_3P)_2Pt\{B(X)X'\}]^+$ compared with the starting materials *trans*-$[(Cy_3P)_2Pt(Br)\{B(X)X'\}]$ (δ in ppm, *J* in Hz).

-B(X)X′		δ(^{31}P) (^1J(P,Pt))		Precursor δ(^{31}P) (^1J(P,Pt))	Anion
X = Fc, X′ = Br[9]	**1**	41.7 (2914)	**2**	21.5 (2892)	$[BAr^f_4]^-$
X = *o*Tol, X′ = Br	**12a, b**	42.2 (2931)	**5**	18.7 (2908)	$[BAr^f_4]^-$, $[B(C_6F_5)_4]^-$
X = *t*Bu, X′ = Br	**13a, b**	41.9 (2979)	**6**	23.7 (2962)	$[BAr^f_4]^-$, $[B(C_6F_5)_4]^-$
X = NMe_2, X′ = Br	**14**	42.8 (2803)	**7**	24.0 (2811)	$[BAr^f_4]^-$
X = Pip, X′ = Br	**15a, b**	43.0 (2845)	**8**	24.6 (2867)	$[BAr^f_4]^-$, $[BPh_4]^-$
X = X′ = Br	**16**	39.5 (2717)	**9**	19.4 (2683)	$[BAr^f_4]^-$
X = X′ = NMe_2	**17**	45.4 (3057)	**10**	27.4 (3067)	$[B(C_6F_5)_4]^-$
XX′ = Cat	**18**	51.2 (2466)	**11**	28.7 (2587)	$[BAr^f_4]^-$



Scheme 2. Formation of cationic boryl complexes by halide abstraction.

Results and Discussion

The boryl complexes *trans*-$[(Cy_3P)_2Pt(Br)\{B(X)X'\}]$ (X = Br, X′ = *o*Tol, *t*Bu, NMe_2, Pip, Br; XX′ = $(NMe_2)_2$, Cat) (**5**–**11**) were reacted with equimolar amounts of $Na[BAr^f_4]$, $K[B(C_6F_5)_4]$ or $Na[BPh_4]$ in dichloromethane at ambient temperature. In all cases the reaction mixtures turned yellow and a fine white solid precipitated (NaBr or KBr) over a period of 2 h. However, the reaction of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Pip\}]$ (**8**) with $Na[BPh_4]$ required sonication for 1 h to solubilize the sodium salt. Multinuclear NMR spectra indicated the quantitative conversion of the starting materials within minutes. All products **12**–**18** are characterized by sharp singlets between $\delta = 39.5$ and 51.2 ppm in the $^{31}P\{^1H\}$ NMR spectra, which are shifted about 20 ppm to lower field when compared to the starting (bromo)boryl complexes **5**–**11** ($\delta = 18.7$–28.7 ppm).[6e] The magnitude of the ^1J(P,Pt) coupling stays constant (largest difference for –BCat: 121 Hz) (Table 1). These findings are in very good agreement with those made for the conversion of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Fc\}]$ (**2**) ($\delta = 21.5$ ppm, ^1J(P,Pt) = 2892 Hz)[6g] into *trans*-$[(Cy_3P)_2Pt\{B(Br)Fc\}][BAr^f_4]$ (**1**) ($\delta = 41.7$ ppm, ^1J(P,Pt) = 2914 Hz),[9] thus indicating similar T-shaped geometries and the presence of boryl groups for **12**–**18** (Scheme 2). It has to be noted that the magnitude of the ^1J(P,Pt) coupling constant of the compounds reflects the *trans*-influence of the corresponding boryl ligand, that is, the larger the coupling constant, the larger the *trans*-influence and the stronger the σ-donating properties of the boryl ligand. For example, compound **17** exhibits the boryl ligand

with the strongest and **18** the one with the weakest *trans*-influence accompanied by a smaller ^1J(P,Pt) coupling constant and a shorter Pt–B bond length (Tables 1 and 2).[7] In contrast, the formation of the borylene complex is accompanied by a significantly reduced coupling constant ($\delta = 45.0$ ppm, $^1J(P,Pt) = 2072$ Hz) in comparison to its precursor *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)Mes\}]$ (**3**) ($\delta = 18.9$ ppm, $^1J(P,Pt) = 3054$ Hz).[6f]

Table 2. Selected bond lengths [Å] and angles [°] in the cationic boryl complexes (short Pt···H(C) and Pt···C distances; hydrogen atoms were assigned to idealized positions).

-B(X)X′		Pt–B	Pt···H(C)	Pt···C	P-Pt-P
X = Fc, X′ = Br[9]	**1**	1.966(4)	2.542	3.117	162.96(3)
X = *o*Tol, X′ = Br	**12a**	1.972(2)	2.384	3.056	168.09(6)
X = *t*Bu, X′ = Br	**13b**	1.957(3)	2.467	3.174	157.26(2)
X = NMe_2, X′ = Br	**14**	1.987(4)	2.498	3.390	168.08(3)
X = Pip, X′ = Br	**15a**	1.989(3)	2.380	3.031	166.36(2)
X = X′ = Br	**16**	1.932(4)	2.481	3.084	167.44(3)
X = X′ = NMe_2	**17**	2.047(5)	2.826	3.399	169.85(4)
XX′ = Cat	**18**	1.977(7)	2.322	2.923	171.84(6)

The $^{11}B\{^1H\}$ NMR spectra of **12–18** all exhibit a sharp signal for the four-coordinate boron atom of the anion ($[BAr^f_4]^-$: $\delta = -7.6$ ppm; $[B(C_6F_5)_4]^-$: $\delta = -17.6$ ppm; $[BPh_4]^-$: $\delta = -7.5$ ppm), whereas the resonance of the Pt-bound boron could only be detected for *trans*-$[(Cy_3P)_2Pt\{B(Br)tBu\}]^+$ (**13**) and *trans*-$[(Cy_3P)_2Pt\{B(Br)oTol\}]^+$ (**12**). The broad signals arise at $\delta =$ 55 and 45 ppm, respectively, and are high-field shifted by about 25 ppm relative to the corresponding neutral complexes (*trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)tBu\}]$ (**6**): $\delta = 80$ ppm; *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)oTol\}]$ (**5**): $\delta = 73$ ppm).[6e] The absence of signals for the other species can be attributed to unresolved coupling to platinum and phosphorus nuclei.[16]

Compounds **12–18** were isolated as analytically pure yellow solids with good yields of 57–78%. They decompose readily when exposed to air and moisture but can be stored as solids under argon for months. Crystals suitable for X-ray analyses were obtained by layering solutions of the complexes in CD_2Cl_2 with hexane and cooling at −35 °C (Figure 1).

The crystal structures confirm T-shaped geometries around the platinum centers for all cationic complexes. The platinum atoms are surrounded by three ligands and a free coordination site is located *trans* to the boryl group. In accordance with the decreased coordination number of the metal center, the Pt–B distances are approximately 3 pm shorter than in the neutral complexes.

The most remarkable structural feature of these cationic species is the presence of a three coordinate Pt^{II} center. It is well known that unsaturated Lewis acidic metal fragments in 14-electron d^8 ML_3 systems show high reactivity, including interactions with weak nucleophiles, such as solvent molecules or weakly coordinating anions,[10,11a,17] and agostic C–H interactions.[11b,12–14,18] In the solid state all cationic compounds **12–18** show no solvent molecules coordinating to

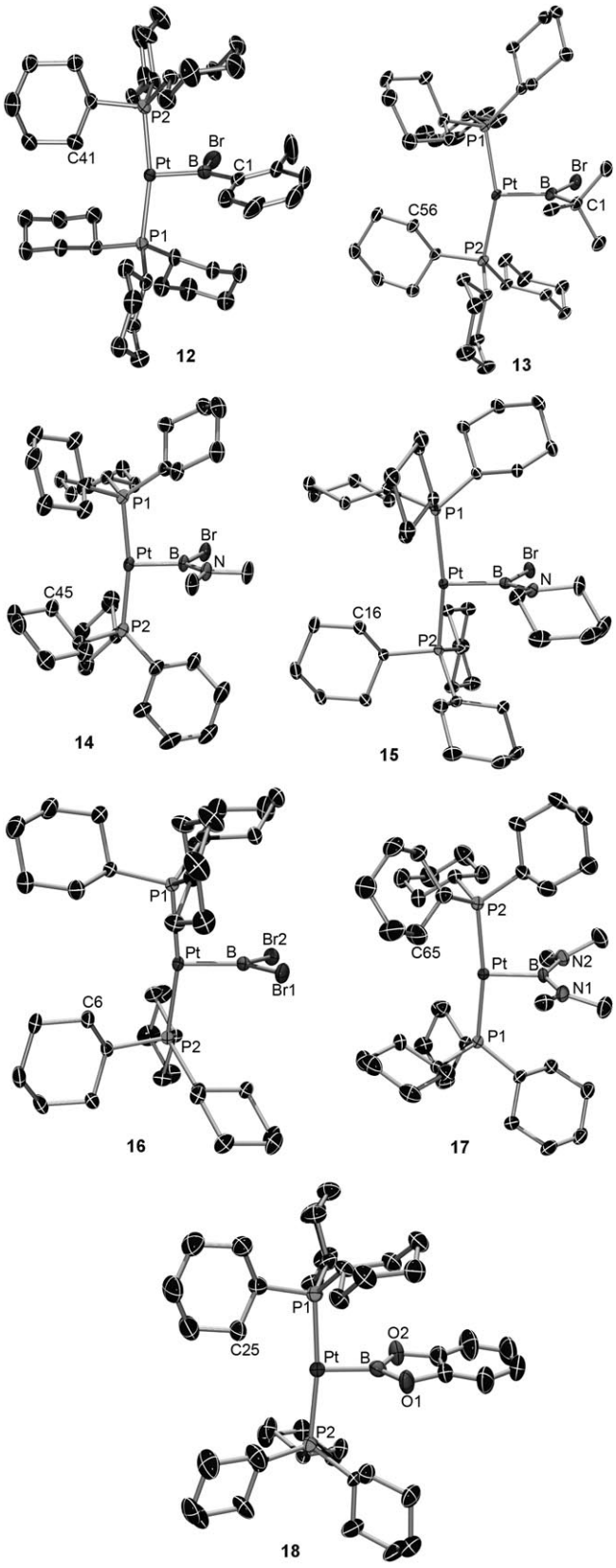


Figure 1. Molecular structures of the cationic boryl complexes **12–18**. Anions, hydrogen atoms, and cocrystallized solvent molecules (**12**: $2CH_2Cl_2$; **13**: $0.5C_6H_{14}$; **14**: $2C_6H_{14}$; **15**: $2CH_2Cl_2$; **17**: CH_2Cl_2; **18**: $2CH_2Cl_2$) are omitted for clarity. The boryl groups in **12** and **14** are disordered. Thermal ellipsoids represent 50% probability. Important bond lengths and angles are shown in Table 2.

the Pt center, and the shortest distances between Pt atoms and H or C atoms of the cyclohexyl groups are larger than in complexes with notable agostic interactions (Table 2). The −BCat ligand, which exhibits the weakest *trans*-influence in the series of neutral complexes, understandably imposes the closest Pt···H(C) and Pt···C interactions (2.322 and 2.923 Å). However, these distances are still somewhat greater than those in $[PtMe(P\mathit{i}Pr_3)_2][1\text{-H-}\mathit{closo}\text{-}CB_{11}Me_{11}]$ (Pt···H(C) = 2.24 Å, Pt···C = 2.859 Å),[13] or $[Pt\text{–}\{P(2,6\text{-}Me_2C_6H_3)Cy_2\}\{\kappa^2\text{-}P,C\text{-}P(2\text{-Me-}6\text{-}CH_2\text{-}C_6H_3)Cy_2\}][BAr^f{}_4]$ (Pt···C = 2.432 Å).[14] Therefore there is little structural evidence for a significant agostic interaction.

It should be noted that theoretical calculations on 14-electron d^8 ML_3 boryl complexes of the type $[(R_3P)_2Rh(BX_2)]$ corroborate that C–H bonds preferably do not coordinate *trans* to the boryl moiety, owing to the huge *trans*-influence of the latter.[19] The absence of any agostic interaction in the case of *trans*-$[(Cy_3P)_2Pt\{B(Br)Fc\}][BAr^f{}_4]$ (**1**) was not only proven by structural and DFT studies but also by low-temperature NMR spectroscopy in solution,[9] and *trans*-$[(Cy_3P)_2Pt(BCat)][BAr^f{}_4]$ (**18**) was subjected to corresponding variable-temperature NMR spectroscopy studies on account of its conspicuously short Pt···H–(C) and Pt···C separations compared to **1**, and **12**–**17**.

At room temperature the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at $\delta = 51.1$ ppm ($^1J(P,Pt) = 2460$ Hz), whereas cooling of the sample to −40 °C leads to a broadening of the signals (maximum intensity at $\delta = 48$ ppm) and coalescence. Further cooling to −80 °C results in sharper resonances displaying two doublets at $\delta = 60.0$ ppm ($^1J(P,Pt) \approx 2303$ Hz, $^2J(P,Pt) = 258$ Hz) and $\delta = 49.9$ ppm ($^1J(P,Pt) \approx 2381$ Hz, $^2J(P,Pt) = 258$ Hz) as well as another singlet at $\delta = 46.9$ ppm ($^1J(P,Pt) \approx 2500$ Hz). The two doublets show a distinct "Dacheffekt" (Figure 3) and indicate an agostic interaction of the Pt center (Pt···H(C)) with a C–H bond of the cyclohexyl group (Figure 2). Because of the agostic interaction, chemical equivalence of both PCy_3 ligands is canceled and the original singlet ($\delta = 51.1$ ppm) splits into two doublets as the inequivalent phosphine moieties couple to each other. The new signal at $\delta = 46.9$ ppm was tentatively assigned to a CD_2Cl_2 adduct (**19**) of the T-shaped boryl complex **18**. Attempts to detect a corresponding resonance in the $^{13}C\{^1H\}$ NMR spectrum failed, owing to unresolved coupling to two deuterium,[20] a platinum, and two phosphorus nuclei.

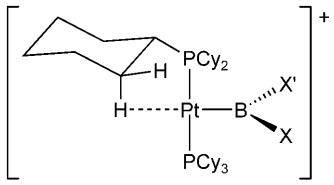


Figure 2. Schematic illustration of an agostic interaction of a C–H bond of the cyclohexyl group with the Pt^{II} center.

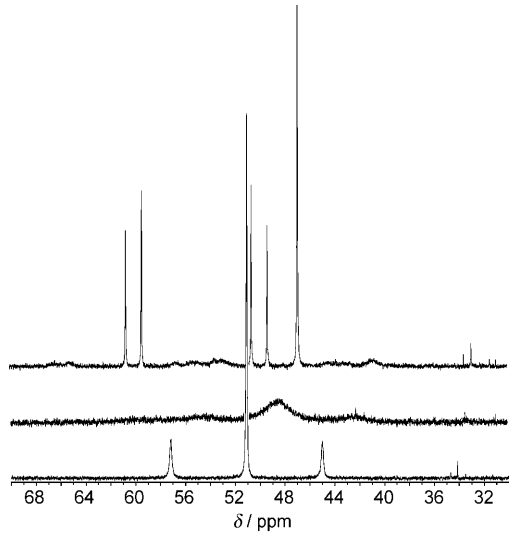
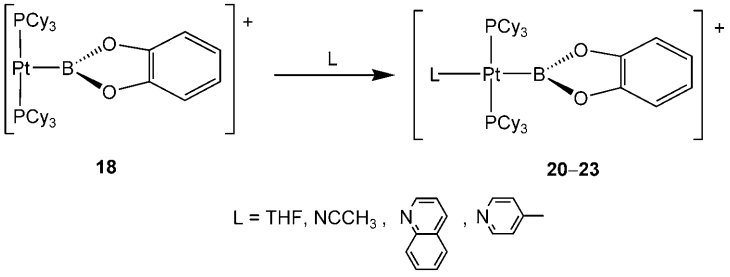


Figure 3. Temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[(Cy_3P)_2Pt(BCat)][BAr^f{}_4]$ (**18**) (bottom: room temperature; middle: −40 °C; top: −60 °C).

At −60 °C the ^1H NMR spectrum features low-field shifted ($\delta = 3.29$ ppm (m); $\delta = 2.57$ ppm (m)) as well as high-field shifted signals ($\delta = -0.52$ ppm (m)), which presumably can be attributed to the proton of the agostic Pt···H(C) interaction. Because of the presence of two different compounds in the sample and inconsistent NMR shifts reported in the literature for agostic hydrogen atoms,[11b,20,21] it is difficult to assign the resonances unambiguously. Remarkably, only one set of signals is observed for the catechol group ($\delta = 7.23$ (brs) and 7.04 ppm (brs)). Warming of the sample to room temperature affords exactly the same NMR spectroscopy data as prior to the low-temperature experiment. To determine whether the $^{31}P\{^1H\}$ NMR spectroscopy shift of $\delta = 46.9$ ppm ($^1J(P,Pt) \approx 2500$ Hz) is connected with the formation of a CD_2Cl_2 adduct (**19**), $^{31}P\{^1H\}$ NMR spectroscopy resonances of the T-shaped complex *trans*-$[(Cy_3P)_2Pt(BCat)][BAr^f{}_4]$ (**18**) were measured in the presence of various Lewis bases. Thus **18** was treated with THF, acetonitrile, quinoline, and 4-methylpyridine (Scheme 3). The THF adduct (**20**) shows a signal at $\delta = 45.6$ ppm ($^1J(P,Pt) \approx 2759$ Hz), however, a 1000-fold excess of THF was necessary to convert half of the starting material. The complex



Scheme 3. Reaction of *trans*-$[(Cy_3P)_2Pt(BCat)][BAr^f{}_4]$ (**18**) with Lewis bases.

with acetonitrile (**21**) exhibits a chemical shift of $\delta =$ 29.4 ppm (^1J(P,Pt) $\approx$ 2532 Hz); the reaction with quinoline (**22**) reveals a signal at $\delta = 26.5$ ppm (^1J(P,Pt) = 2507 Hz) and with 4-methylpyridine (**23**) at $\delta = 26.9$ ppm (^1J(P,Pt) = 2520 Hz).

The chemical shift of the THF adduct as well as the coupling constants of all base adducts **20**–**23** are in line with the formation of the CD_2Cl_2 adduct **19** at low temperatures. Moreover, several related dichloromethane adducts are already reported in the literature.[17,22] *trans*-[$(Cy_3P)_2Pt(NC_5H_4$-4-Me)(BCat)][BAr^f_4] (**23**) could be fully characterized and isolated in 73% yield as a colorless, air- and moisture-sensitive solid. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a CH_2Cl_2/hexane mixture (Figure 4).

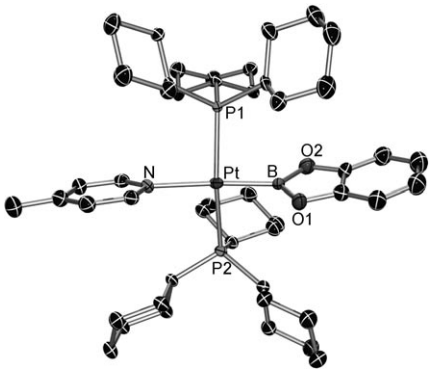


Figure 4. Molecular structure of *trans*-[$(Cy_3P)_2Pt(NC_5H_4$-4-Me)(BCat)]-[BAr^f_4] (**23**). The unit cell of **23** contains two independent molecules. In one of them the catechol boryl group and the 4-methylpyridine ligand are disordered, therefore the structural parameters of the other molecule are discussed. The disordered molecule, anions, hydrogen atoms, and co-crystallized solvent molecules ($2C_6H_{14}$) are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [°]: Pt–B 2.013(5), Pt–N 2.220(5), B–O1 1.387(6), B–O2 1.387(5), P1-Pt-P2 165.15(5), P1-Pt-B-O1 103.5(4), P1-Pt-N-C2 91.3(4), N-Pt-B-O1 9.2(14).

Compound **23** displays a slightly distorted square-planar geometry around the platinum center. The planes of the 4-methylpyridine and the catechol boryl moiety are mutually twisted by 9° (N-Pt-B-O1 9.2(14)°). The Pt–B bond (Pt–B 2.013(5) Å) is longer than in the cationic boryl complex **18** (Pt–B 1.977(7) Å) but shorter than in the bromoboryl species *trans*-[$(Cy_3P)_2Pt(Br)(BCat)$] (**11**) (2.048(6) Å), which can be attributed to the coordination number of four and the positive charge at the Pt center in **23**. The *trans*-influence of the boryl moiety is indicated by a relatively long Pt–N bond (2.220(5) Å). Pt–N distances in comparable complexes commonly lie around 2.10 Å (e.g., *trans*-[$(Ph_3P)_2Pt(\eta^1$-1,4-N_2-C_4H_3-2-Cl)(C_4H_4-2-S)] 2.082(4) Å).[23]

To investigate the exceptional behavior of *trans*-[$(Cy_3P)_2Pt(Br)${B(Br)Mes}] towards Na[BAr^f_4] or K[B-(C_6F_5)$_4$], the reaction was carried out at −80 °C and monitored by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 5). At −80 °C a singlet is observed at $\delta = 41.2$ ppm (^1J(P,Pt) = 2999 Hz)

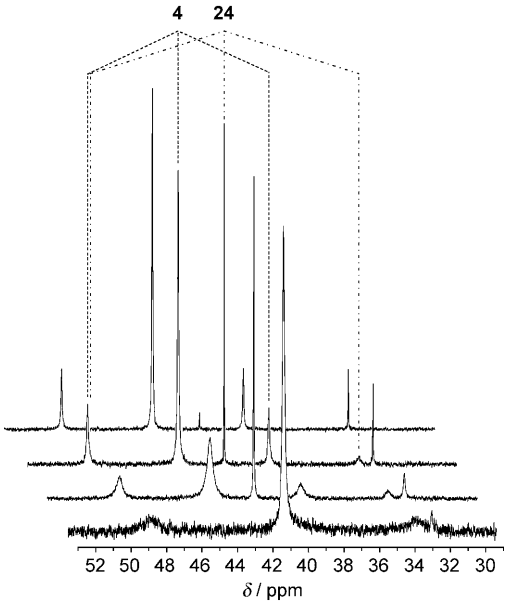
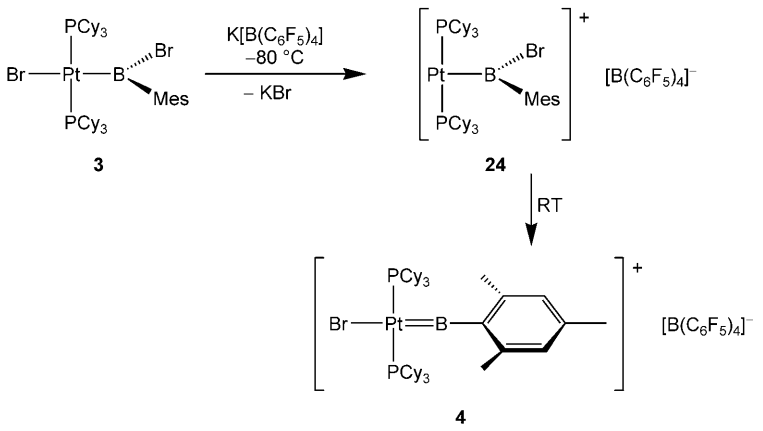


Figure 5. Temperature-dependent formation of *trans*-[$(Cy_3P)_2Pt(Br)$-(BMes)][$B(C_6F_5)_4$] (**4**) and *trans*-[$(Cy_3P)_2Pt${B(Br)Mes}][$B(C_6F_5)_4$] (**24**) observed in the $^{31}P\{^1H\}$ NMR spectrum (bottom: −60 °C; second from bottom: −20 °C; second from top: 10 °C; top: room temperature).

flanked by platinum satellites bearing a coupling constant differing strongly from the isolated complex *trans*-[$(Cy_3P)_2Pt(Br)(BMes)]^+$ (**4**) ($\delta = 45.0$ ppm (^1J(P,Pt) = 2072 Hz))[6f] (the small signal at $\delta = 33.0$ ppm can be assigned to the byproduct [$HPCy_3$][$B(C_6F_5)_4$],[24] which is often observed under similar conditions). Warming to −40 °C leads to the build-up of another singlet at $\delta = 44.3$ ppm (^1J-(P,Pt) = 2070 Hz), with increasing intensity by further warming, whereas the intensity of the resonance at $\delta = 41.2$ ppm decreases. The signal at $\delta = 44.3$ ppm can be assigned to the isolated borylene complex [$(Cy_3P)_2Pt(Br)(BMes)$][$B(C_6F_5)_4$] (**4**),[6f] whereas the slightly high-field shifted signal is indicative of the formation of the T-shaped boryl complex *trans*-[$(Cy_3P)_2Pt${B(Br)Mes}][$B(C_6F_5)_4$] (**24**) (Scheme 4).

In the ^1H NMR spectrum two temperature-dependent sets of signals can be detected for the mesityl group (T-shaped isomer **24**: $\delta = 6.88$ (1H; CH), 6.85 (1H; CH), 2.95 (3H; CH_3^{ortho}), 2.47 (3H; CH_3^{ortho}), 2.18 ppm (3H; CH_3^{para}); borylene isomer **4**: $\delta = 6.95$ (2H; CH), 2.63 (6H; CH_3^{ortho}), 2.29 ppm (3H; CH_3^{para})).[6f] At room temperature the T-shaped boryl complex **24** is converted almost completely to the borylene isomer **4**. If the probe is cooled again, the ratio of both compounds does not change, therefore an equilibrium between the two forms can be excluded. Hence, the reaction of *trans*-[$(Cy_3P)_2Pt(Br)${B(Br)Mes}] with Na[BAr^f_4] or K[$B(C_6F_5)_4$] is consistent with the behavior of other boryl complexes of the type *trans*-[$(Cy_3P)_2Pt(Br)${B(Br)X}], in which the bromide is abstracted at the platinum center with concomitant formation of a T-shaped boryl complex. In the case of *trans*-[$(Cy_3P)_2Pt(Br)${B(Br)X}], the T-shaped boryl intermediate **24** rearranges by a formal 1,2-bromide shift from the boron atom to the platinum center with formation



Scheme 4. Formation of *trans*-[$(Cy_3P)_2$Pt(Br)(BMes)] (**4**) from **3** via *trans*-[$(Cy_3P)_2$Pt{B(Br)Mes}]$^+$ (**24**).

of the thermodynamically more stable borylene species **4** (Scheme 4).

A similar 1,2-bromide shift was observed for **1** when adding the Lewis base 4-methylpyridine, forming *trans*-[$(Cy_3P)_2$Pt(Br){B(NC_5H_4-4-Me)Fc}][BAr^f_4].[9] Another example of this kind of behavior was noted in the synthesis of some osmium borylene compounds[25] and appears to be a useful tool for the synthesis of borylene complexes.

Conclusion

In conclusion, the synthesis of a range of cationic T-shaped Pt^{II} complexes *trans*-[$(Cy_3P)_2$Pt{B(X)X′}]$^+$ could be achieved by halide abstraction from *trans*-[$(Cy_3P)_2$Pt(Br){B(X)X′}]. All complexes were fully characterized and the crystal structures show relatively long Pt···H(C) and Pt···C distances. Furthermore, no solvent molecules are occupying the vacant site at ambient temperature, thus emphasizing the strong *trans*-influence imposed by most of the employed boryl ligands. However, low-temperature NMR spectra of *trans*-[$(Cy_3P)_2$Pt(BCat)][BAr^f_4], which among the series of new complexes is characterized by the shortest Pt···H(C) and Pt···C separations, reveals typical resonances for an agostic interaction at −60 °C, as well as a signal for a dichloromethane adduct. The somewhat decreased *trans*-influence of the BCat ligand reflected by these findings was further corroborated by the formation of adducts upon reaction of *trans*-[$(Cy_3P)_2$Pt(BCat)][BAr^f_4] with the Lewis bases THF, acetonitrile, quinoline, and 4-methylpyridine, thus proving the influence of the boryl ligand on the reactivity of the title compounds. The product of the latter reaction was isolated and fully characterized in solution and in the solid state. To elucidate the different behavior of *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)Mes}] towards halide abstraction, the reaction was carried out at low temperatures and monitored by NMR spectroscopy. Comparison of the NMR spectroscopy data revealed that initial abstraction of the bromide at the platinum center occurs with formation of a transient T-shaped boryl complex. Upon warming, a formal 1,2-bromide shift takes place, yielding the borylene species *trans*-[$(Cy_3P)_2$Pt(Br)(BMes)]$^+$ as the final product.

Experimental Section

General description for the preparation of cationic boryl complexes: Equimolar amounts of the neutral boryl complexes **5**–**11** and Na[BAr^f_4] or K[$B(C_6F_5)_4$] were loaded into a J. Young NMR spectroscopy tube and CD_2Cl_2 (0.6 mL) was added. The reaction mixtures turned immediately yellow and a fine white solid (NaBr/KBr) precipitated. After 2 h the suspension was filtered and the filtrate was layered with hexane (1–2 mL). After one week at −35 °C yellow crystals of the cationic boryl complexes **12**–**18** had formed.

***trans*-[$(Cy_3P)_2$Pt{B(Br)*o*Tol}][BAr^f_4] (12a)**: *trans*-[$(Cy_3P)_2$Pt{B(Br)*o*Tol}][BAr^f_4] (0.031 g, 65 %) was obtained after one day from the reaction of Na[BAr^f_4] (0.024 g, 0.027 mmol) and *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)*o*Tol}] (**5**) (0.027 g, 0.027 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): δ = 8.37 (d, ^3J(H,H) = 8 Hz, 1H; CH^{ortho}, Tol), 7.74 (m, 8H; BAr^f_4), 7.58 (brs, 4H; BAr^f_4), 7.49 (dd, ^3J(H,H) = 7 and 8 Hz, 1H; CH^{para}, Tol), 7.32 (dd, ^3J(H,H) = 7 Hz, 1H; C^{meta}, Tol), 7.26 (d, ^3J(H,H) = 8 Hz, 1H; CH^{meta}, Tol), 2.93 (s, 3H; CH_3, Tol), 2.26 (m, 6H; Cy), 2.05–1.97 (m, 6H; Cy), 1.89–1.69 (m, 24H; Cy), 1.60–1.42 (m, 12H; Cy), 1.25–1.15 ppm (m, 18H; Cy); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 24 °C): δ = 162.2 (q, ^1J(C,B) = 50 Hz; C^{ipso}, BAr^f_4), 143.5 (s; C^{ortho}, Tol; 2D-HMBC), 141.0 (s; C^{ortho}, Tol), 137.5 (brs; C^{ipso}, Tol; 2D-HMQC), 135.2 (s; C^{ortho}, BAr^f_4), 133.8 (s; C^{para}, Tol), 132.6 (s; C^{meta}, Tol; 2D-HMQC), 129.3 (qq, ^2J(C,F) = 31 Hz, ^3J(C,B) = 3 Hz; C^{meta}, BAr^f_4), 126.0 (s; C^{meta}, Tol; 2D-HMQC), 125.0 (q, ^1J(C,F) = 272 Hz; CF_3, BAr^f_4), 117.9 (sep, ^3J(C,F) = 4 Hz; C^{para}, BAr^f_4), 34.9 (vt, N = |^1J(C,P) + ^3J(C,P)| = 27 Hz; C^1, Cy), 30.7 (s; $C^{3,5}$, Cy), 30.5 (s; $C^{3,5}$, Cy), 27.4 (brs; $C^{2,6}$, Cy), 26.1 (s; C^4, Cy), 25.6 ppm (s; CH_3, Tol); ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 24 °C): δ = 45 (brs; PtB), −7.5 ppm (s; BAr^f_4); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 24 °C): δ = 42.2 ppm (s, ^1J(P,Pt) = 2936 Hz); elemental analysis calcd (%) for $C_{75}H_{85}B_2BrF_{24}P_2Pt$: C 50.13, H 4.54; found: C 50.47, H 4.83.

***trans*-[$(Cy_3P)_2$Pt{B(Br)*o*Tol}][$B(C_6F_5)_4$] (12b)**: *trans*-[$(Cy_3P)_2$Pt{B(Br)*o*Tol}][$B(C_6F_5)_4$] was obtained as a yellow solid (0.019 g, 47 %) by evaporation of the solvent of a reaction mixture of K[$B(C_6F_5)_4$] (0.018 g, 0.025 mmol) and *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)*o*Tol}] (**5**) (0.025 g, 0.025 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.37 (d, ^3J(H,H) = 8 Hz, 1H; C^6, Tol), 7.51 (dd, ^3J(H,H) = 7 and 8 Hz, 1H; C^4, Tol), 7.32 (dd, ^3J(H,H) = 7 Hz, 1H; C^5, Tol), 7.26 (d, ^3J(H,H) = 8 Hz, 1H; C^3, Tol), 2.93 (s, 3H; CH_3, Tol), 2.26 (m, 6H; Cy), 2.08–1.98 (m, 6H; Cy), 1.90–1.70 (m, 24H; Cy), 1.62–1.42 (m, 12H; Cy), 1.25–1.15 ppm (m, 18H; Cy); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 25 °C): δ = 148.5 (brd, ^1J(C,F) = 241 Hz; C^{para}, $B(C_6F_5)_4$), 143.4 (s; C^2, Tol; 2D-HMBC), 140.9 (s; C^6, Tol), 138.5 and 136.6 (2 overlapping brd, ^1J(C,F) = 243 Hz; $C^{ortho,meta}$, $B(C_6F_5)_4$), 137.5 (brs; C^1, Tol; 2D-HMBC), 133.7 (s; C^4, Tol), 132.5 (s; C^3, Tol; 2D-HMQC), 125.9 (s; C^5, Tol; 2D-HMQC), 124.1 (brs; C^{ipso}, $B(C_6F_5)_4$), 34.8 (vt, N = |^1J(C,P) + ^3J(C,P)| = 27 Hz; C_1, Cy), 30.6 (s; $C^{3,5}$, Cy), 30.4 (s; $C^{3,5}$, Cy), 27.3 (brs; $C^{2,6}$, Cy), 26.0 (s; C^4, Cy), 25.5 ppm (s; CH_3, Tol); ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 25 °C): δ = 45.0 (brs; PtB), −17.6 ppm (s; $B(C_6F_5)_4$); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 25 °C): δ = 42.2 ppm (s, ^1J(P,Pt) = 2931 Hz); elemental analysis calcd (%) for $C_{67}H_{73}B_2BrF_{20}P_2Pt$: C 49.77, H 4.55; found: C 50.87, H 5.19.

***trans*-[$(Cy_3P)_2$Pt{B(Br)*t*Bu}][BAr^f_4] (13a)**: *trans*-[$(Cy_3P)_2$Pt{B(Br)*t*Bu}][BAr^f_4] (0.028 g, 78 %) was prepared from *trans*-[$(Cy_3P)_2$Pt(Br){B(Br)*t*Bu}] (**6**) (0.020 g, 0.020 mmol) and Na[BAr^f_4] (0.018 g, 0.020 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): δ = 7.73 (m, 8H; BAr^f_4), 7.57 (brs, 4H; BAr^f_4), 2.28–2.21 (m, 6H; Cy), 2.08–2.02 (m,

6H; Cy), 1.96–1.88 (m, 18H; Cy), 1.82–1.70 (m, 12H; Cy), 1.64–1.55 (m, 6H; Cy), 1.35–1.26 (m, 18H; Cy), 1.21 ppm (s, 9H; *t*Bu); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): $\delta = 162.0$ (q, $^1J(C,B) = 50$ Hz; C^{ipso}, BAr^f_4), 135.1 (s; C^{ortho}, BAr^f_4), 129.2 (qq, $^2J(C,F) = 31$ Hz, $^3J(C,B) = 3$ Hz; C^{meta}, BAr^f_4), 124.9 (q, $^1J(C,F) = 272$ Hz; CF_3, BAr^f_4), 117.7 (sep, $^3J(C,F) = 4$ Hz; C^{para}, BAr^f_4), 36.4 (brs; C, *t*Bu), 35.8 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 26$ Hz; C^1, Cy), 30.7 (s; $C^{3,5}$, Cy), 30.3 (s; $C^{3,5}$, Cy), 30.0 (s; CH_3, *t*Bu), 27.6–27.4 (2 overlapping vt; $C^{2,6}$, Cy), 26.0 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta = 55.2$ (brs; PtB), −7.6 ppm (s, BAr^f_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 41.9$ ppm (s, $^1J(P,Pt) = 2985$ Hz); elemental analysis calcd (%) for $C_{72}H_{87}B_2BrF_{24}P_2Pt$: C 48.94, H 4.96; found: C 49.37, H 4.92.

***trans*-[(Cy$_3$P)$_2$Pt{B(Br)*t*Bu}][B(C$_6$F$_5$)$_4$] (13b)**: The reaction of K[B(C$_6$F$_5$)$_4$] (0.018 g, 0.025 mmol) with *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)*t*Bu}] (**6**) (0.025 g, 0.025 mmol) leads to *trans*-[(Cy$_3$P)$_2$Pt{B(Br)*t*Bu}][B(C$_6$F$_5$)$_4$], which was isolated after four weeks (0.023 g, 57 %). ^1H NMR (500 MHz, CD_2Cl_2, 23 °C): $\delta = 2.25$ (m, 6H; Cy), 2.08–2.02 (m, 6H; Cy), 1.96–1.88 (m, 18H; Cy), 1.82–1.70 (m, 12H; Cy), 1.64–1.55 (m, 6H; Cy), 1.35–1.26 (m, 18H; Cy), 1.21 ppm (s, 9H; *t*Bu); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): $\delta = 148.5$ (brd, $^1J(C,F) = 235$ Hz; C^{para}, $B(C_6F_5)_4$), 138.5 and 136.6 (2 overlapping brd, $^1J(C,F) = 243$ Hz; $C^{ortho,meta}$, $B(C_6F_5)_4$), 124.1 (brs; C^{ipso}, $B(C_6F_5)_4$), 36.4 (brs; C, *t*Bu), 35.8 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 26$ Hz; C^1, Cy), 30.7 (s; $C^{3,5}$, Cy), 30.3 (s; $C^{3,5}$, Cy), 30.0 (s; CH_3, *t*Bu), 27.6–27.4 (2 overlapping vt; $C^{2,6}$, Cy), 26.0 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 23 °C): $\delta = 55.2$ (brs; PtB), −17.6 ppm (s; $B(C_6F_5)_4$); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): $\delta = 41.9$ ppm (s, $^1J(P,Pt) = 2979$ Hz); elemental analysis calcd (%) for $C_{72}H_{87}B_2BrF_{24}P_2Pt$: C 48.56, H 4.78; found: C 48.69, H 4.65.

***trans*-[(Cy$_3$P)$_2$Pt{B(Br)NMe$_2$}][BAr$^f_4$] (14)**: The reaction of *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)NMe$_2$}] (**7**) (0.030 g, 0.031 mmol) and Na[BAr$^f_4$] (0.027 g, 0.031 mmol) led to *trans*-[(Cy$_3$P)$_2$Pt{B(Br)NMe$_2$}][BAr$^f_4$] (0.031 g, 57 %). ^1H NMR (500 MHz, CD_2Cl_2, 23 °C): $\delta = 7.73$ (m, 8H; BAr^f_4), 7.57 (brs, 4H; BAr^f_4), 3.22 (s, 3H; NMe_2), 2.86 (s, 3H; NMe_2), 2.33 (m, 6H; Cy), 2.07–2.01 (m, 6H; Cy), 1.92–1.86 (m, 18H; Cy), 1.82–1.75 (m, 6H; Cy), 1.63–1.46 (m, 12H; Cy), 1.39–1.22 ppm (m, 18H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 23 °C): $\delta = 162.0$ (q, $^1J(C,B) = 50$ Hz; C^{ipso}, BAr^f_4), 135.1 (s; C^{ortho}, BAr^f_4), 129.2 (qq, $^2J(C,F) = 31$ Hz, $^3J(C,B) = 3$ Hz; C^{meta}, BAr^f_4), 124.9 (q, $^1J(C,F) = 273$ Hz; CF_3, BAr^f_4), 117.7 (sep, $^3J(C,F) = 4$ Hz; C^{para}, BAr^f_4), 46.4 (s; NMe_2), 40.5 (s; NMe_2), 35.0 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 27$ Hz; C^1, Cy,), 30.7 (s; $C^{3,5}$, Cy), 30.2 (s; $C^{3,5}$, Cy), 27.6–27.4 (2 overlapping vt; $C^{2,6}$, Cy), 26.2 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 23 °C): $\delta = -7.6$ ppm (s; BAr^f_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 23 °C): $\delta = 42.8$ ppm (s, $^1J(P,Pt) = 2803$ Hz); elemental analysis calcd (%) for $C_{70}H_{84}NB_2BrF_{24}P_2Pt$: C 47.93, H 4.83, N 0.80; found: C 47.70, H 4.81, N 0.89.

***trans*-[(Cy$_3$P)$_2$Pt{B(Br)Pip}][BAr$^f_4$] (15a)**: *trans*-[(Cy$_3$P)$_2$Pt{B(Br)Pip}][BAr$^f_4$] (0.025 g, 70 %) was obtained as a yellow solid after 3 d by evaporation of the solvent from a reaction mixture of *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)Pip}] (**8**) (0.020 g, 0.020 mmol) and Na[BAr$^f_4$] (0.018 g, 0.020 mmol). Single crystals were formed by recrystallization from CD_2Cl_2/hexane at −35 °C. ^1H NMR (500 MHz, CD_2Cl_2, 24 °C): $\delta = 7.73$ (m, 8H; BAr^f_4), 7.57 (m, 4H; BAr^f_4), 3.69 (m, 2H; NCH_2, Pip), 3.37 (m, 2H; NCH_2, Pip), 2.35 (m, 6H; Cy), 2.05–1.75 (m, 30H; Cy), 1.70–1.60 (m, 4H; 2 CH_2, Pip), 1.58–1.50 (m, 12H; Cy), 1.48–1.42 (m, 2H; CH_2, Pip), 1.38–1.22 ppm (m, 18H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): $\delta = 162.0$ (q, $^1J(C,B) = 50$ Hz; C^{ipso}, BAr^f_4), 135.1 (s; C^{ortho}, BAr^f_4), 129.1 (qq, $^2J(C,F) = 32$ Hz, $^3J(C,B) = 3$ Hz; C^{meta}, BAr^f_4), 124.9 (q, $^1J(C,F) = 272$ Hz; CF_3, BAr^f_4), 117.7 (sep, $^3J(C,F) = 4$ Hz; C^{para}, BAr^f_4), 55.6 (s; NCH_2, Pip), 50.7 (s; NCH_2, Pip), 35.0 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 26$ Hz; C^1, Cy), 30.6 (s; $C^{3,5}$, Cy), 30.5 (s; $C^{3,5}$, Cy), 27.6–27.4 (2 overlapping vt; $C^{2,6}$, Cy), 27.1 (s; CH_2, Pip), 26.2 (s; CH_2, Pip), 26.1 (s; C^4, Cy), 24.9 ppm (s; CH_2, Pip); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta = -7.6$ ppm (s; BAr^f_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 43.0$ ppm (s, $^1J(P,Pt) = 2846$ Hz); elemental analysis calcd (%) for $C_{73}H_{88}NB_2BrF_{24}P_2Pt$: C 48.87, H 4.94, N 0.78; found: C 49.23, H 4.84, N 0.79.

***trans*-[(Cy$_3$P)$_2$Pt{B(Br)Pip}][BPh$_4$] (15b)**: *trans*-[Br(Cy$_3$P)$_2$Pt{B(Br)Pip}] (**8**) (0.015 g, 0.015 mmol) and Na[BPh$_4$] (0.005 g, 0.015 mmol) were loaded in a J. Young NMR spectroscopy tube and CD_2Cl_2 (0.6 mL) was added. The reaction mixture was sonicated for 1 h, turned yellow, and a fine solid precipitated. The suspension was filtered after 1 d and layered with hexane (2 mL) and the solvent was allowed to evaporate slowly. After 2 d *trans*-[(Cy$_3$P)$_2$Pt{B(Br)Pip}][BPh$_4$] was isolated (0.012 g, 65 %). ^1H NMR (500 MHz, CD_2Cl_2, 24 °C): $\delta = 7.32$ (m, 8H; BPh_4), 7.04 (m, 8H; BPh_4), 6.89 (m, 4H; BPh_4), 3.70 (m, 2H; NCH_2, Pip),), 3.38 (m, 2H; NCH_2, Pip), 2.33 (m, 6H; Cy), 2.08–1.22 ppm (m, 60+6H; Cy+3CH_2, Pip); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): $\delta = 164.3$ (q, $^1J(C,B) = 49$ Hz; C^{ipso}, BPh_4), 136.2 (q, $^2J(C,B) = 1$ Hz; C^{ortho}, BPh_4), 125.9 (q, $^3J(C,B) = 3$ Hz; C^{meta}, BPh_4), 121.9 (s; C^{para}, BPh_4), 55.6 (s; NCH_2, Pip), 50.7 (s; NCH_2, Pip), 35.0 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 27$ Hz; C^1, Cy), 30.6 (s; $C^{3,5}$, Cy), 30.5 (s; $C^{3,5}$, Cy), 27.6–27.4 (2 overlapping vt; $C^{2,6}$, Cy), 27.1 (s; CH_2, Pip), 26.2 (s; CH_2, Pip), 26.1 (s; C^4, Cy), 24.9 ppm (s; CH_2, Pip); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta = -7.5$ ppm (s; BPh_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 43.0$ ppm (s, $^1J(P,Pt) = 2845$ Hz); elemental analysis calcd (%) for $C_{65}H_{96}NB_2BrP_2Pt$: C 62.45, H 7.74, N 1.12; found: C 63.17, H 7.60, N 1.12.

***trans*-[(Cy$_3$P)$_2$Pt(BBr$_2$)][BAr$^f_4$] (16)**: The reaction of *trans*-[(Cy$_3$P)$_2$Pt(Br)(BBr$_2$)] (**9**) (0.020 g, 0.020 mmol) and Na[BAr$^f_4$] (0.018 g, 0.020 mmol) led to *trans*-[(Cy$_3$P)$_2$Pt(BBr$_2$)][BAr$^f_4$] (0.024 g, 67 %). ^1H NMR (500 MHz, CD_2Cl_2, 21 °C): $\delta = 7.73$ (m, 8H; BAr^f_4), 7.57 (brs, 4H; BAr^f_4), 2.37 (m, 6H; Cy), 1.95–1.85 (m, 24H; Cy), 1.83–1.76 (m, 6H; Cy), 1.68–1.58 (m, 12H; Cy), 1.35–1.25 ppm (m, 18H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 21 °C): $\delta = 162.0$ (q, $^1J(C,B) = 50$ Hz; C^{ipso}, BAr^f_4), 135.1 (s; C^{ortho}, BAr^f_4), 129.1 (qq, $^2J(C,F) = 31$ Hz, $^3J(C,B) = 3$ Hz; C^{meta}, BAr^f_4), 124.9 (q, $^1J(C,F) = 272$ Hz; CF_3, BAr^f_4), 117.7 (sep, $^3J(C,F) = 4$ Hz; C^{para}, BAr^f_4), 34.8 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 27$ Hz; C^1, Cy), 30.2 (s; $C^{3,5}$, Cy), 27.3 (vt, $N = |^2J(C,P) + {}^4J(C,P)| = 12$ Hz; $C^{2,6}$, Cy), 25.9 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ 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): $\delta = 39.5$ ppm (s, $^1J(P,Pt) = 2717$ Hz); elemental analysis calcd (%) for $C_{68}H_{78}B_2Br_2F_{24}P_2Pt$: C 45.63, H 4.39; found: C 45.73, H 4.34.

***trans*-[(Cy$_3$P)$_2$Pt{B(NMe$_2$)$_2$}][B(C$_6$F$_5$)$_4$] (17)**: Yellow crystals of *trans*-[(Cy$_3$P)$_2$Pt{B(NMe$_2$)$_2$}][B(C$_6$F$_5$)$_4$] (0.019 g, 73 %) were obtained from *trans*-[(Cy$_3$P)$_2$Pt(Br){B(NMe$_2$)$_2$}] (**10**) (0.016 g, 0.017 mmol) and K[B(C$_6$F$_5$)$_4$] (0.012 g, 0.017 mmol) after two weeks at −35 °C. ^1H NMR (500 MHz, CD_2Cl_2, 21 °C): $\delta = 2.81$ (s, 12H; NMe_2), 2.18 (m, 6H; Cy), 2.02–1.97 (m, 12H; Cy), 1.90–1.85 (m, 12H; Cy), 1.79–1.74 (m, 6H; Cy), 1.56–1.46 (m, 12H; Cy), 1.36–1.22 ppm (m, 18H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 21 °C): $\delta = 148.5$ (brd, $^1J(C,F) = 242$ Hz; C^{para}, B(C$_6$F$_5$)$_4$), 138.5 and 136.6 (2 overlapping brd, $^1J(C,F) = 242$ Hz; $C^{ortho,meta}$, $B(C_6F_5)_4$), 124.2 (brs; C^{ipso}, $B(C_6F_5)_4$), 42.3 (s; NMe_2), 35.1 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 26$ Hz; C^1, Cy), 30.7 (s; $C^{3,5}$, Cy), 27.7 (vt, $N = |^2J(C,P) + {}^4J(C,P)| = 11$ Hz; $C^{2,6}$, Cy), 26.3 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 21 °C): $\delta = -17.6$ ppm (s; $B(C_6F_5)_4$); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 21 °C): $\delta = 45.4$ ppm (s, $^1J(P,Pt) = 3051$ Hz); elemental analysis calcd (%) for $C_{64}H_{78}B_2F_{20}N_2P_2Pt{\cdot}CH_2Cl_2$: C 48.23, H 4.98, N 1.73; found: C 48.82, H 5.10, N 1.79.

***trans*-[(Cy$_3$P)$_2$Pt(BCat)][BAr$^f_4$] (18)**: The reaction of *trans*-[(Cy$_3$P)$_2$Pt(Br)(BCat)] (**11**) (0.020 g, 0.021 mmol) and Na[BAr$^f_4$] (0.018 g, 0.021 mmol) allowed for the isolation of *trans*-[(Cy$_3$P)$_2$Pt(BCat)][BAr$^f_4$] (0.023 g, 63 %). ^1H NMR (500 MHz, CD_2Cl_2, 24 °C): $\delta = 7.73$ (m, 8H; BAr^f_4), 7.57 (brs, 4H; BAr^f_4), 7.27–7.22 (m, 2H; Cat), 7.12–7.07 (m, 2H; Cat), 2.29 (m, 6H; Cy), 1.95–1.87 (m, 12H; Cy), 1.80–1.70 (m, 18H; Cy), 1.60–1.50 (m, 12H; Cy), 1.38–1.22 ppm (m, 18H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): $\delta = 162.1$ (q, $^1J(C,B) = 50$ Hz; C^{ipso}, BAr^f_4), 148.2 (s; $C^{1,2}$, Cat), 135.2 (s; C^{ortho}, BAr^f_4), 129.3 (qq, $^2J(C,F) = 31$ Hz, $^3J(C,B) = 3$ Hz; C^{meta}, BAr^f_4), 125.0 (q, $^1J(C,F) = 273$ Hz; CF_3, BAr^f_4), 123.5 (s; $C^{4,5}$, Cat), 117.8 (sep, $^3J(C,F) = 4$ Hz; C^{para}, BAr^f_4), 112.6 (s; $C^{3,6}$, Cat), 35.8 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 27$ Hz; C^1, Cy), 30.5 (s; $C^{3,5}$, Cy), 28.0 (vt, $N = |^2J(C,P) + {}^4J(C,P)| = 11$ Hz; $C^{2,6}$, Cy), 26.3 ppm (s; C^4, Cy); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta = -7.6$ ppm (s; BAr^f_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 51.1$ ppm (s, $^1J(P,Pt) = 2464$ Hz); elemental analysis calcd (%) for $C_{74}H_{82}B_2F_{24}O_2P_2Pt$: C 51.14, H 4.76; found: C 51.02, H 4.91.

Spectroscopic characterization of *trans*-[(Cy$_3$P)$_2$Pt(THF)(BCat)][BAr$^f_4$] (20): *trans*-[(Cy$_3$P)$_2$PtBCat][BAr$^f_4$] (**18**) (0.013 g, 0.007 mmol) was loaded

into a J. Young NMR spectroscopy tube and dissolved in CD_2Cl_2 (0.6 mL). Two drops of THF were added and $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of a new signal, yet the peaks for the starting material were still present. More THF was added to increase the intensity of the new peak, which can be most likely assigned to *trans*-[$(Cy_3P)_2$Pt(THF)(BCat)][BAr^f_4]. However, a huge excess of THF leads only to a ratio of 2:1 for the starting material and the product in the ^1H NMR spectrum. ^1H NMR (200 MHz, CD_2Cl_2, 21 °C): $\delta = 7.71$ (m, 12H; BAr^f_4), 7.54 (brs, 6H; BAr^f_4), 7.23 (m, 2H; Cat, **51**), 7.07 (m, 2H; Cat, **51**), 7.02 (m, 1H; Cat, **54**), 6.92 (m, 1H; Cat, **54**), 3.68 (m, 900H; free THF), 1.80 (m, 900H; free THF), 2.40–1.10 ppm (m, Cy); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 51.1$ (s, ^1J(P,Pt) = 2464 Hz; **51**), 45.6 ppm (s, ^1J(P,Pt) = 2467 Hz; **54**).

Spectroscopic characterization of *trans*-[$(Cy_3P)_2$Pt(NCMe)(BCat)][BAr^f_4] (21): *trans*-[$(Cy_3P)_2$PtBCat][BAr^f_4] (**18**) (0.010 g, 0.006 mmol) was loaded in a J. Young NMR spectroscopy tube and dissolved in CH_2Cl_2 (0.5 mL) and C_6D_6 (0.1 mL). Then one drop of NCMe was added to the yellow solution. $^{31}P\{^1H\}$ NMR spectroscopy showed complete consumption of the starting material and the formation of a predominant compound, which was most likely *trans*-[$(Cy_3P)_2$Pt(NCMe)(BCat)][BAr^f_4]. ^1H NMR (200 MHz, C_6D_6/CH_2Cl_2, 21 °C): $\delta = 7.77$ (m, 8H; BAr^f_4), 7.59 (brs, 4H; BAr^f_4), 7.36 (s, C_6D_6), 7.17 (m, 2H; Cat), 7.02 (m, 2H; Cat), 1.93 (s, 59H; free NCMe), 2.50–0.90 ppm (m, Cy); $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 21 °C): $\delta = 31.4$ ppm (s, ^1J(P,Pt) = 2532 Hz).

Spectroscopic characterization of *trans*-[$(Cy_3P)_2$Pt(NC_9H_7)(BCat)][BAr^f_4] (22): *trans*-[$(Cy_3P)_2$Pt(Br)(BCat)] (**18**) (0.020 g, 0.021 mmol) and Na[BAr^f_4] (0.018 g, 0.021 mmol) were converted into *trans*-[$(Cy_3P)_2$Pt(BCat)][BAr^f_4]. In a J. Young NMR spectroscopy tube in CD_2Cl_2 (0.5 mL) quinoline (0.004 g, 0.031 mmol) was added to the yellow reaction mixture. $^{31}P\{^1H\}$ NMR spectroscopy showed the consumption of the starting material and the formation of a new main product, which was most likely *trans*-[$(Cy_3P)_2$Pt(NC_9H_7)(BCat)][BAr^f_4]. ^1H NMR (200 MHz, CD_2Cl_2, 21 °C): $\delta = 9.10$–7.35 (complex superpositions, free and bound quinoline), 7.73 (m, 8H; BAr^f_4), 7.56 (brs, 4H; BAr^f_4), 7.25 (m, 2H; Cat), 7.10 (m, 2H; Cat), 2.40–0.50 ppm (m; Cy); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 21 °C): $\delta = 26.5$ ppm (s, ^1J(P,Pt) = 2507 Hz).

***trans*-[$(Cy_3P)_2$Pt(NC_5H_4-4-CH_3)(BCat)][BAr^f_4] (23)**: *trans*-[$(Cy_3P)_2$Pt(Br)(BCat)] (**18**) (0.015 g, 0.016 mmol) and Na[BAr^f_4] (0.014 g, 0.016 mmol) were converted into *trans*-[$(Cy_3P)_2$Pt(BCat)][BAr^f_4] in CD_2Cl_2 (0.6 mL) in a J. Young NMR spectroscopy tube. After removing NaBr by filtration, NC_5H_4-4-CH_3 (0.001 g, 0.016 mmol) was added to the solution. Over the course of one day the reaction mixture turned colorless and was layered with hexane (2 mL). Slow evaporation of the solvent led to the formation of crystals of *trans*-[$(Cy_3P)_2$Pt(NC_5H_4-4-CH_3)(BCat)][BAr^f_4] (0.028 g, 73%). ^1H NMR (500 MHz, CD_2Cl_2, 24 °C): $\delta =$ 8.50 (d, ^3J(H,H) = 6 Hz; MePyr), 7.73 (d, ^3J(H,H) = 6 Hz 8H; BAr^f_4), 7.57 (brs, 4H; BAr^f_4), 7.45 (m; NC_5H_4-4-CH_3), 7.20 (m, 2H; Cat), 7.05 (m, 2H; Cat), 2.51 (s, 3H; CH_3, NC_5H_4-4-CH_3), 1.82–1.60 (m, 36H; Cy), 1.51 (m, 12H; Cy), 1.20 (m, 6H; Cy), 0.90 ppm (m, 12H; Cy); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 24 °C): $\delta = 162.0$ (q, ^1J(C,B) = 50 Hz; C^{ipso}, BAr^f_4), 152.6 (s; C^{ipso}, NC_5H_4-4-CH_3), 151.6 (s; C^{ortho}, NC_5H_4-4-CH_3), 148.9 (s; $C^{1,2}$, Cat), 135.1 (s; C^{ortho}, BAr^f_4), 129.1 (qq, ^2J(C,F) = 32 Hz, ^3J(C,B) = 3 Hz; C^{meta}, BAr^f_4), 127.7 (s; C^{meta}, NC_5H_4-4-CH_3), 124.9 (q, ^1J(C,F) = 272 Hz; CF_3, BAr^f_4), 122.5 (s; $C^{4,5}$, Cat), 117.7 (sep, ^3J(C,F) = 4 Hz; C^{para}, BAr^f_4), 111.9 (s; $C^{3,6}$, Cat), 35.8 (vt, $N = |^1J(C,P) + {}^3J(C,P)| = 28$ Hz; C^1, Cy), 30.3 (s; $C^{3,5}$, Cy), 27.9 (vt, $N = |^2J(C,P) + {}^4J(C,P)| = 11$ Hz; $C^{2,6}$, Cy), 26.5 (s; C^4, Cy), 21.4 ppm (s; CH_3, NC_5H_4-4-CH_3); $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 24 °C): $\delta = -7.6$ ppm (s; BAr^f_4); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 24 °C): $\delta = 26.9$ ppm (s, ^1J(P,Pt) = 2520 Hz); elemental analysis calcd (%) for $C_{80}H_{89}NB_2F_{24}O_2P_2Pt$: C 52.47, H 4.90, N 0.76; found: C 52.06, H 5.06, N 0.72.

Crystal structure determination: The crystal data of **12**–**16** were collected using a Bruker x8 APEX diffractometer with multi-layer mirror monochromated $Mo_{K\alpha}$ radiation, and those of **17**–**18** using a Bruker SMART APEX with graphite monochromated $Mo_{K\alpha}$ radiation. Both diffractometers were equipped with CCD area detectors. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations. The crystals of **15** and **17** had voids with badly disordered DCM (180 Å^3 and 135 Å^3, respectively). The crystallographic refinement for these two structures was completed with the solvent contribution subtracted from the data using SQUEEZE from the PLATON package of crystallographic software.[26]

Crystal data for **12**: $C_{80}H_{96}B_2BrCl_4F_{24}P_2Pt$; $M_r = 2013.93$; yellow plate; $0.22 \times 0.13 \times 0.02$ mm^3; monoclinic space group $C2/c$; $a = 39.219(9)$, $b = 12.724(3)$, $c = 33.981(8)$ Å; $\beta = 96.715(12)°$; $V = 16842(7)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.589$ g cm^{-3}; $\mu = 2.402$ mm^{-1}; $F(000) = 8104$; $T = 99(2)$ K; $R_1 = 0.1052$; $wR^2 = 0.2046$; 24743 independent reflections [$2\theta = 62.1°$] and 1194 parameters.

Crystal data for **13**: $C_{64}H_{75}B_2BrF_{20}P_2Pt$; $M_r = 1582.80$; colorless plate; $0.40 \times 0.28 \times 0.12$; triclinic space group $P\bar{1}$; $a = 12.2890(9)$, $b = 15.0446(11)$, $c = 17.9045(14)$ Å; $\alpha = 99.636(4)$, $\beta = 94.737(4)$, $\gamma = 92.908(4)°$; $V = 3245.4(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.620$ g cm^{-3}; $\mu = 2.924$ cm^{-2}; $F(000) = 1584$; $T = 97(2)$ K; $R_1 = 0.0450$; $wR^2 = 0.0705$; 19805 independent reflections [$2\theta = 62.76°$] and 811 parameters.

Crystal data for **14**: $C_{82}H_{112}B_2BrF_{24}NP_2Pt$; $M_r = 1926.29$; yellow block; $0.18 \times 0.16 \times 0.06$; triclinic space group $P\bar{1}$; $a = 11.9350(6)$, $b = 17.9683(10)$, $c = 20.1949(11)$ Å; $\alpha = 86.094(2)$, $\beta = 88.373(2)$, $\gamma = 85.844(2)°$; $V = 4308.2(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.485$ g cm^{-3}; $\mu = 2.224$ cm^{-2}; $F(000) = 1960$; $T = 100(2)$ K; $R_1 = 0.0615$; $wR^2 = 0.1479$; 37687 independent reflections [$2\theta = 70.72°$] and 1148 parameters.

Crystal data for **15**: $C_{75}H_{92}B_2BrCl_4F_{24}NP_2Pt$; $M_r = 1963.86$; colorless plate; $0.28 \times 0.10 \times 0.02$; triclinic space group $P\bar{1}$; $a = 12.7575(6)$, $b = 17.5303(7)$, $c = 19.2578(9)$ Å; $\alpha = 94.370(2)$, $\beta = 90.359(2)$, $\gamma = 100.373(2)°$; $V = 4223.3(3)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.544$ g cm^{-3}; $\mu = 2.392$ mm^{-1}; $F(000) = 1972$; $T = 100(2)$ K; $R_1 = 0.0457$; $wR^2 = 0.0793$; 27654 independent reflections [$2\theta = 66.2°$] and 1011 parameters.

Crystal data for **16**: $C_{68}H_{78}B_2Br_2F_{24}P_2Pt$; $M_r = 1789.77$; colorless block; $0.14 \times 0.15 \times 0.41$; triclinic space group $P\bar{1}$; $a = 14.2842(4)$, $b = 14.6245(4)$, $c = 18.6421(5)$ Å; $\alpha = 86.290(1)$, $\beta = 71.124(1)$, $\gamma = 80.960(2)°$; $V = 3638.72(17$ Å^3; $Z = 2$; $\rho_{calcd} = 1.634$ g cm^{-3}; $\mu = 3.171$ mm^{-1}; $F(000) = 1780$; $T = 100(2)$ K; $R_1 = 0.0575$; $wR^2 = 0.1039$; 26118 independent reflections [$2\theta = 69.14°$] and 922 parameters.

Crystal data for **17**: $C_{65}H_{80}B_2Cl_2F_{20}P_2Pt$; $M_r = 1618.86$; yellow block; $0.10 \times 0.10 \times 0.06$; triclinic space group $P\bar{1}$; $a = 11.1831(4)$, $b = 15.1659(6)$, $c = 20.4196(7)$ Å; $\alpha = 87.802(1)$, $\beta = 77.636(1)$, $\gamma = 83.402(1)°$; $V = 3360.1(2)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.600$ g cm^{-3}; $\mu = 2.313$ mm^{-1}; $F(000) = 1632$; $T = 173(2)$ K; $R_1 = 0.0470$; $wR^2 = 0.1132$; 13265 independent reflections [$2\theta = 52°$] and 820 parameters.

Crystal data for **18**: $C_{76}H_{86}B_2Cl_2F_{24}O_2P_2Pt$; $M_r = 1907.90$; yellow block; $0.30 \times 0.18 \times 0.12$; triclinic space group $P\bar{1}$; $a = 14.4625(11)$, $b = 14.6991(11)$, $c = 20.3510(15)$ Å; $\alpha = 83.368(1)$, $\beta = 75.983(1)$, $\gamma = 89.955(1)°$; $V = 4167.8(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.520$ g cm^{-3}; $\mu = 1.947$ mm^{-1}; $F(000) = 1920$; $T = 173(2)$ K; $R_1 = 0.0730$; $wR^2 = 0.1381$; 18422 independent reflections [$2\theta = 52°$] and 1084 parameters.

Crystal data for **23**: $C_{86}H_{103}B_2F_{24}NO_2P_2Pt$; $M_r = 1917.34$; yellow block; $0.18 \times 0.12 \times 0.09$; triclinic space group $P\bar{1}$; $a = 12.9195(7)$, $b = 23.3819(12)$, $c = 29.2613(16)$ Å; $\alpha = 82.381(3)$, $\beta = 84.920(3)$, $\gamma = 83.984(3)°$; $V = 8688.0(8)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.466$ g cm^{-3}; $\mu = 1.750$ mm^{-1}; $F(000) = 3904$; $T = 100(2)$ K; $R_1 = 0.0860$; $wR^2 = 0.1728$; 34043 independent reflections [$2\theta \leq 52.34°$] and 2309 parameters.

CCDC-687218, 687219, 687220, 687221, 687222, 687223, 687224, and 69144 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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