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# Experimental Studies on the *trans*-Influence of Boryl Ligands in Square-Planar Platinum(II) Complexes

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**Abstract:** A series of platinum(II) boryl complexes of general formula *trans*-[$(Cy_3P)_2Pt(Br)(BX_2)$], including the rare dibromoboryl species *trans*-[$(Cy_3P)_2Pt(Br)(BBr_2)$], were synthesized by oxidative addition of the B–Br bond of a number of bromoboranes to [$Pt(PCy_3)_2$]. X-ray diffraction studies were performed on several such compounds. Comparison of the Pt–Br bond lengths allowed an empirical assessment of the *trans*-influence of different boryl ligands. A *trans*-influence scale was thus deduced and the results were compared with those previously computed for compounds of the type *trans*-[$(Me_3P)_2Pt(Cl)(BX_2)$].

**Keywords:** boron · boryl complexes · oxidative addition · platinum · *trans*-influence

Transition-metal boryl complexes are known to act as intermediates in important catalytic processes, such as the metal-catalyzed hydroboration[1] and diboration[2] of unsaturated organic compounds, as well as the catalyzed selective functionalization of C–H bonds of alkanes, arenes, and heteroarenes.[3] Consequently, significant research effort has been devoted to the optimization of a number of synthetic routes to these compounds,[4] to the study of their structural properties and reactivity, as well as to the theoretical elucidation of the nature of the bonding interactions that link the boron center to the transition metal.[5] The resulting experimental work led to the isolation of boryl complexes of most transition metals, featuring a variety of substituents at boron, with the catechol group (Cat = phenylene-1,2-dioxo) being the most common; alkyl, aryl or halide residues, on the contrary, being relatively rare.[4e] The results of a large number of structural investigations allowed the high *trans*-influence exerted by boryl ligands in their transition metal complexes to be deduced.[4] Indeed, on account of its strong σ-donor character, the boryl ligand displays a higher *trans*-labilizing ability[6] than that of other σ donors, such as hydrido[7a,c] and stannyl[7b] groups, or π acceptors like carbon monoxide,[7d,e] as judged by the long *trans*-TM–X bond lengths (TM = transition metal). The origin of this property was further investigated theoretically. Hence, comparing the structural parameters of the optimized computed molecular structures of compounds *trans*-[$(Me_3P)_2Pt(Cl)(Boryl)$], Marder and Lin were able to unveil the strong dependence of the *trans*-influence of different boryl ligands on their σ-donor properties.[5d] They also confirmed the higher *trans*-labilizing ability of boryl ligands with respect to other good σ donors, such as hydride, silyl, and carbon-based groups, whose high *trans*-influence is generally recognized.

Platinum boryl complexes,[4b,e] particularly of the type *cis*-[$(R_3P)_2Pt(BX_2)_2$], are numerous, in view of their involvement in the platinum-catalyzed diboration of organic substrates.[2] Our work on platinum bromoboryl complexes led to the straightforward synthesis of *trans*-[$(Cy_3P)_2Pt(Br)\{B(Br)Fc\}$] (**1**) (Fc = Ferrocenyl) upon oxidative addition of a B–Br bond of $FcBBr_2$ to [$Pt(PCy_3)_2$].[8a] The very high *trans*-influence of the -B(Br)Fc group allowed the generation of the cationic platinum complex *trans*-[$(Cy_3P)_2Pt\{B(Br)Fc\}$][$BAr^f_4$] (**2**) ($Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$), upon bromide abstraction at platinum in **1** with Na[$BAr^f_4$], and contributed to the isolation of **2** as the first T-shaped cationic platinum complex devoid of any stabilizing agostic interaction.[8b] This experimental finding paralleled the theoretical conclusions drawn by Marder and Lin in their studies on rhodium-catalyzed borylation of aromatic C–H bonds, where 14-electron $d^8ML_3$ boryl complexes of the type [$(R_3P)_2Rh(BX_2)$] were calculated to be reluctant to bind

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C−H bonds in the site *trans* to the boryl group, due to the extremely strong *trans*-influence of the latter.[9]

In continuation of our work on platinum(II) boryl complexes, we wondered to what extent the *trans*-influence of the boryl ligand in such compounds could be fine-tuned by changing the nature of the substituents at boron, and set out to synthesize a range of compounds of the type *trans*-[$(Cy_3P)_2Pt(Br)\{B(Br)X\}$] following the same synthetic protocol that led to the isolation of **1**. Herein we report the full analytical, spectroscopic, and structural characterization of such compounds, of *trans*-[$(Cy_3P)_2Pt(Br)(BCat')$] (Cat′ = Cat-4-*t*Bu) and *trans*-[$(Cy_3P)_2Pt(Br)\{B(NMe_2)_2\}$], and compare the *trans*-influence data thus determined with those of other boron-based ligands and with the previously computed ones. From a synthetic point of view, the isolation and structural characterization of *trans*-[$(Cy_3P)_2Pt(Br)(BBr_2)$] is particularly noteworthy.[10] Only a handful of dihaloboryl complexes were previously structurally authenticated.[4e] However, such compounds were proven to be versatile precursors to a number of unusual molecular systems. For instance, the dichloroboryl complex [$Os(BCl_2)Cl(CO)(PPh_3)_2$][7e] could be readily converted into the first base-stabilized borylene compound [$Os(=BNHC_9H_6N)Cl_2(CO)(PPh_3)_2$][7e] and into a variety of tethered boryl complexes of osmium,[11a] whereas the dihaloboryl species [$(\eta^5\text{-}C_5R_5)Fe(CO)_2(BX_2)$] (R = H, Me; X = Cl, Br) were employed as precursors to the metalloborylene complexes [$(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu_2\text{-}B)M(CO)_n$] (M = Cr, $n=5$; M = Fe, $n=4$),[11b] the boryl-bridged compound [$(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)_2(\mu\text{-}BCl_2)Pd(PCy_3)$],[11c] and the heterodinuclear bridging borylene complex [$(\eta^5\text{-}C_5Me_5)Fe(CO)(\mu\text{-}CO)(\mu\text{-}BBr)PdBr(PCy_3)$].[11d]

Compounds *trans*-[$(Cy_3P)_2Pt(Br)\{B(Br)X\}$] (X = Fc, **1**;[8a] Mes, (Mes = 2,4,6-$(CH_3)_3C_6H_2$) **3**;[12] o-Tol, **4**; *t*Bu, **5**; Br, **6**; $NMe_2$, **7**; Pip (Pip = $NC_5H_{10}$), **8**), *trans*-[$(Cy_3P)_2Pt(Br)(BCat)$] (**9**), *trans*-[$(Cy_3P)_2Pt(Br)(BCat')$] (**10**), and *trans*-[$(Cy_3P)_2Pt(Br)\{B(NMe_2)_2\}$] (**11**) were prepared by oxidative addition of a B−Br bond of the corresponding bromoboranes to [$Pt(PCy_3)_2$]. Mixing equimolar amounts of the reagents in $C_6D_6$ generally led to completion of the reaction within 1 h, as indicated by multinuclear NMR spectroscopy. However, the reaction of [$Pt(PCy_3)_2$] with $BrB(NMe_2)_2$ required one week to reach completion, while the more reactive $BBr_3$ was added at low temperature (−60 °C) in toluene. All complexes are characterized by sharp singlet resonances in the $^{31}P\{^1H\}$ NMR spectra, which range from $\delta = 29.0$ to 18.7 ppm, flanked by platinum satellites ($^1J(P,Pt) = 2587$–$3067$ Hz) (Table 1). The $^{11}B\{^1H\}$ NMR spectra feature a broad resonance, which is downfield-shifted when compared to the spectra for the corresponding boranes (Table 1).

The compounds were isolated as crystalline solids in 61–83 % yield by layering hexane on the reaction mixtures and allowing slow evaporation of the solvents. The complexes with Br-, N-, O-donor groups on boron were found to be relatively stable and could be briefly handled in air, whereas the ones with alkyl or aryl residues proved to be very sensitive and decomposed readily when exposed to air or moisture.

Table 1. NMR data ($\delta$ in ppm; $J$ in Hz) of complexes **1**, **3**–**11**.

| -BXX′ | Compd | $\delta(^{31}P)$ ($^1J(P,Pt)$) | $\delta(^{11}B)$ |
|---|---|---|---|
| X = Fc, X′ = Br | **1** | 21.5 (2892) | 82 |
| X = Mes, X′ = Br | **3** | 18.9 (3054) | 69 |
| X = o-Tol, X′ = Br | **4** | 18.7 (2908) | 73 |
| X = *t*Bu, X′ = Br | **5** | 23.7 (2962) | 80 |
| X = X′ = Br | **6** | 19.4 (2683) | 54 |
| X = $NMe_2$, X′ = Br | **7** | 24.0 (2815) | 30 |
| X = Pip, X′ = Br | **8** | 24.6 (2867) | 32 |
| XX′ = Cat | **9** | 28.7 (2587) | – |
| XX′ = Cat′ | **10** | 29.0 (2609) | 32 |
| X = X′ = $NMe_2$ | **11** | 27.4 (3067) | 28 |

To investigate the *trans*-influence of the different boryl ligands, the Pt−Br distance in the crystallographically determined molecular structures of the compounds was selected as the parameter of choice. Single crystals of compounds **1**,[8a] **3**,[12] **4**–**8**, **10**, and **11** were obtained and analyzed by X-ray diffraction (Figure 1).[13] Selected bond lengths are reported in Table 2. Due to the poor solubility of *trans*-[$(Cy_3P)_2Pt(Br)(BCat)$] (**9**), no single crystal of this compound could be isolated. Therefore, a *tert*-butyl group was introduced on the borane to improve solubility. The corresponding complex, that is, *trans*-[$(Cy_3P)_2Pt(Br)(BCat')$] (**10**), was crystallized successfully.

All complexes display a slightly distorted square-planar geometry around the platinum center, and a *trans*-disposition of the phosphine ligands. The boryl moieties are oriented almost perpendicular to the $PtP_2$ plane and induce a strong *trans*-influence on the platinum-bonded bromide, as indicated by the long Pt−Br distances, which range from 2.5617(10) to 2.6454(4) Å.

Analysis of the structural parameters associated with the optimized computed compounds *trans*-[$(Me_3P)_2Pt(Cl)(Boryl)$] allowed the authors to draw a number of important conclusions.[5d] First, the σ-donating ability of the boryl ligand was calculated to be the major factor in determining the strength of its *trans*-influence, with π-accepting properties having only limited importance. Second, a correlation between the Pt−B and the Pt−Cl bond lengths was revealed, linking short Pt−B bonds to short Pt−Cl bonds, and hence to weak *trans*-influence of the corresponding boryl ligand. Although counterintuitive at first, such a trend was explained by invoking a greater s-character of the boron-based hybrid orbital used in the formation of the Pt−B bond, leading to short Pt−B bond lengths and simultaneously to a decreased electron-releasing character of the boryl ligand, thus determining its weaker *trans*-influence. Third, the presence of electronegative substituents at boron leads to the use of hybrid orbitals with increased s-character in the platinum−boron bond, resulting in a weaker *trans*-influence of the corresponding boryl ligands.

The structural parameters of compounds *trans*-[$(Cy_3P)_2Pt(Br)\{B(Br)X\}$], **1** and **3**–**8**, indicate that the theoretically observed trend that links short Pt−B bonds to short Pt−Br bonds holds true experimentally for subgroups of compounds with similar electronic properties, that is,

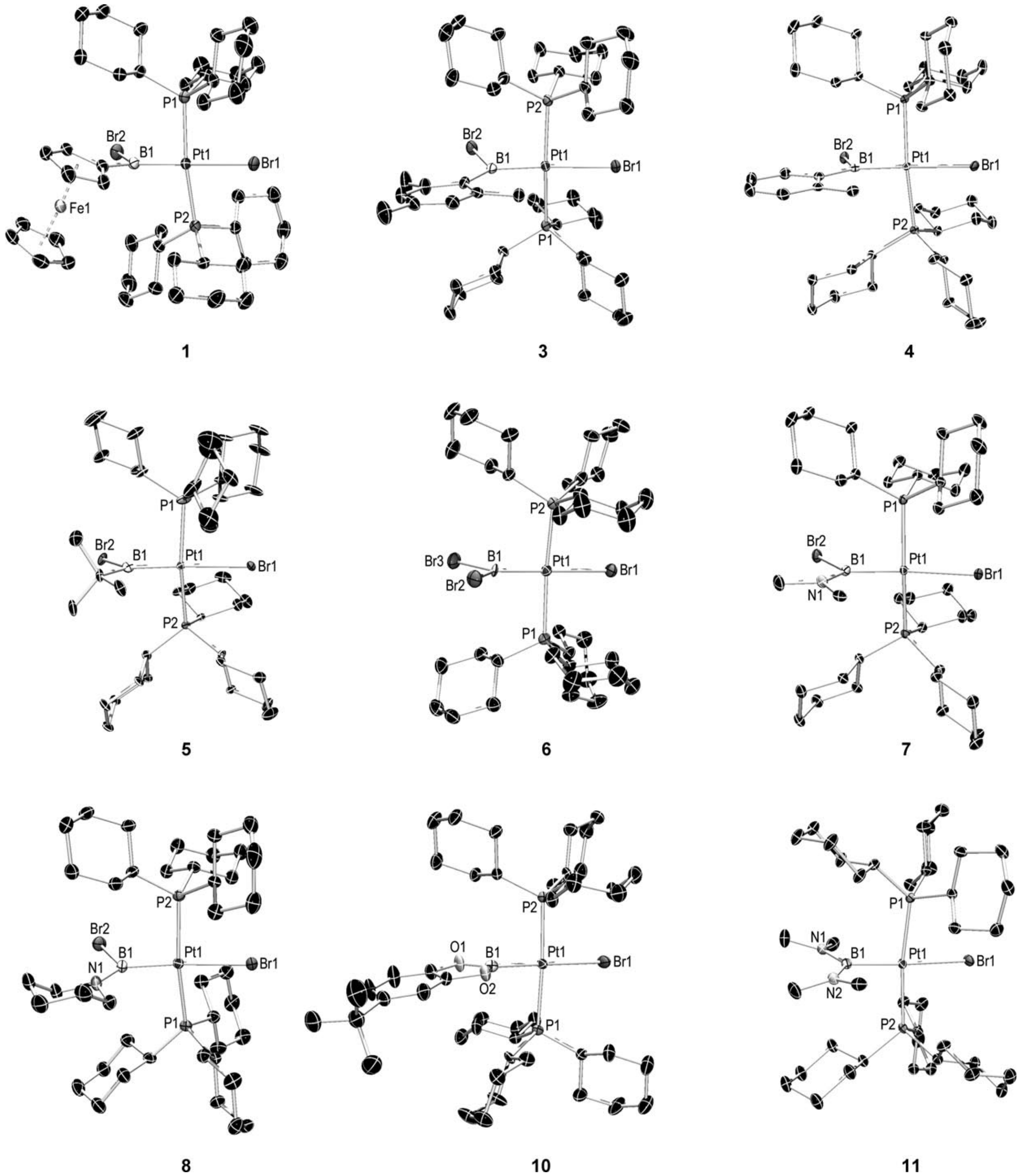

Figure 1. Molecular structures of the boryl complexes **1**, **3**–**8**, **10**, and **11**; solvent molecules are omitted for clarity. The disorder in the $NMe_2$ groups of **10** is omitted for clarity. In the unit cell of **7** two independent molecules were determined. (Ellipsoids at 50 % probability).

-B(Br)Ar (Ar = o-Tol, Fc, Mes) and -B(Br)X (X = $NMe_2$, Pip) (see Table 2). In *trans*-[$(Cy_3P)_2Pt(Br)(BBr_2)$] (**6**), the relatively short Pt–B bond length (1.963(6) Å) is again accompanied by a correspondingly "short" Pt–Br separation (2.5847(6) Å), while the *tert*-butyl(bromo)boryl complex **5**, despite a relatively short Pt–B distance (1.983(5) Å), displays the strongest *trans*-influence (Pt–Br 2.6454(4) Å) being, therefore, somewhat exceptional. Accordingly, the experimentally determined *trans*-influence scale of bromoboryl ligands displayed in Figure 2 can be drawn.

Despite the structural similarity between o-Tol and Mes groups, the *trans*-influence of -B(Br)(o-Tol) and -B(Br)Mes is different. The weaker *trans*-influence of -B(Br)(o-Tol) is accompanied by a longer B–Br bond (2.022(3) Å). Accordingly, a hybrid boron-based orbital with high p-character should be in use for the B–Br bond formation, determining

Table 2. Selected bond lengths [Å] of complexes **1**, **3–8**, **10**, and **11**.

| -BXX′ | Compd | Pt–Br | Pt–B | B–X′ |
|---|---|---|---|---|
| XX′ = Cat′ | **10** | 2.5617(10) | 2.048(6) | 1.368(6) |
| X = X′ = Br | **6** | 2.5847(6) | 1.963(6) | 1.969(6) 1.934(7) |
| X = o-Tol X′ = Br | **4** | 2.5996(3) | 1.982(3) | 2.022(3) |
| X = $NMe_2$ X′ = Br | **7** | 2.6087(3) | 2.009(3) | 2.017(3) |
| X = Fc X′ = Br | **1** | 2.6183(8) | 1.9963(34) | 2.0040(35) |
| X = Mes X′ = Br | **3** | 2.6247(4) | 2.009(4) | 2.006(4) |
| X = X′ = $NMe_2$ | **11** | 2.6252(3) | 2.090(3) | 1.440(2) 1.431(2) |
| X = Pip X′ = Br | **8** | 2.6313(5) | 2.021(5) | 2.024(5) |
| X = *t*Bu X′ = Br | **5** | 2.6454(4) | 1.983(5) | 2.011(4) |

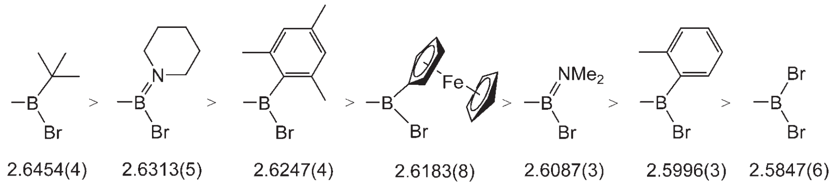

Figure 2. Experimentally determined *trans*-influence scale of bromoboryl ligands (Pt–Br distances are given in Å).

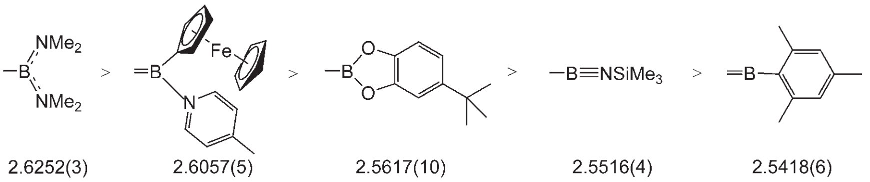

Figure 3. Comparison of the *trans*-influence of different boron-based ligands (Pt–Br bond lengths are given in Å).

a higher s-character in the hybrid orbital engaged in the B–Pt bond, and hence a shorter Pt–Br separation and a weaker *trans*-influence. Generally longer B–Br bonds are observed in boryl ligands that possess electronegative, π-donating substituents (-B(Br)$NMe_2$, 2.017(3) Å; -B(Br)Pip 2.024(5) Å, as opposed to -B(Br)Mes, 2.006(4) Å; -B(Br)Fc, 2.0040(35) Å; -$BBr_2$, 1.969(6) and 1.934(7) Å).

Comparison of the bond lengths in compounds *trans*-[$(Cy_3P)_2$Pt(Br){BCat′}] (**10**) and *trans*-[$(Cy_3P)_2$Pt(Br){B($NMe_2$)$_2$}] (**11**) confirms the trend that relates short Pt–B bonds to short Pt–Br bonds, and hence to weaker *trans*-influence ligands. The -BCat′ group, which induces a Pt–Br separation of 2.5617(10) Å, displays the weakest *trans*-influence of the whole series, while the -B($NMe_2$)$_2$ ligand, bearing the less electronegative nitrogen substituents, exerts a much stronger *trans*-influence, as demonstrated by the long Pt–Br separation of 2.6252(3) Å. Both complexes feature relatively long Pt–B distances, (2.048(6) and 2.090(3) Å, respectively), probably due to the efficient π-donating ability of the heteroatom-based residues, that alleviates the Lewis acidity of the boron atom, thus decreasing the extent of the Pt→B π-backdonation. The presence of residues with less efficient π-donating properties at boron (for instance, Br, o-Tol, and *t*Bu) requires an increased electronic stabilization of the boron center through Pt→B π-backdonation, resulting in relatively short Pt–B distances (1.963(6), **6**; 1.982(3), **4**; 1.983(5) Å, **5**).

Recent work in our laboratories allowed the synthesis and structural characterization of a number of complexes with unprecedented boron-based ligands, such as the iminoboryl complex *trans*-[$(Cy_3P)_2$Pt(Br)(B≡$NSiMe_3$)] (**12**),[14] the terminal borylene complex *trans*-[$(Cy_3P)_2$Pt(Br)(BMes)][B($C_6F_5$)$_4$] (**13**),[12] and the base-stabilized borylene complex *trans*-[$(Cy_3P)_2$Pt(Br){B($NC_5H_4$-4-$CH_3$)Fc}][$BAr^f_4$] (**14**).[8b] Comparison of the Pt–Br bond lengths of these complexes (2.5516(4) Å, **12**; 2.5418(6) Å, **13**; 2.6057(5) Å, **14**, respectively) with those observed in compounds **1**, **3–8**, **10**, **11** indicates the generally stronger *trans*-influence of the -BXX′ groups, with the relatively long Pt–Br separation in **14** being ascribable to the boryl character of the base-stabilized borylene ligand, in view of the three-coordinate boron center (Figure 3).[8b]

In conclusion, boryl complexes of platinum of the type *trans*-[$(Cy_3P)_2$Pt(Br){B(X)X′}] could be obtained by oxidative addition of a B–Br bond of the corresponding bromoboranes to [Pt($PCy_3$)$_2$]. The structural analysis of the compounds allowed a comparison of the Pt–Br bond lengths and hence the assessment of the *trans*-influence of the different boryl ligands. Accordingly, the following *trans*-influence scale could be determined: -BCat′ < -$BBr_2$ < -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. Such experimentally identified order finds a reasonable correlation with that obtained theoretically by Marder and Lin. Since inspection of the crystal packing does not reveal any noticeable intermolecular interaction that may influence the observed bond lengths, small discrepancies may be attributed to the different ancillary phosphine and halide ligands utilized in the experimental and theoretical works.

## Experimental Section

All manipulations were performed under an atmosphere of dry argon or in vacuo using standard Schlenk-line and glove-box techniques. Toluene, benzene, and hexane were purified by distillation over sodium under dry argon and stored under the same inert gas over molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were referenced to external TMS via the residual protio-solvent ($^1H$) or the solvent itself ($^{13}C$). $^{11}B\{^1H\}$ NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and $^{31}P\{^1H\}$ NMR spectra to 85% $H_3PO_4$. Microanalyses were performed on a Leco CHNS-932 Elemental

Analyzer. Complexes *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)Fc}] (**1**)[8a] and *trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)Mes}] (**3**)[12] were prepared according to literature procedures.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)(*o*-Tol)}] (*o*-Tol = C$_6$H$_4$-2-CH$_3$) (4)**: [Pt(PCy$_3$)$_2$] (0.060 g, 0.079 mmol) was dissolved in C$_6$H$_6$ (1.0 mL), and Br$_2$B(*o*-Tol) (0.021 g, 0.079 mmol) was added to the solution. After 24 h the reaction mixture was layered with hexane (1.5 mL) and the solvent was allowed to evaporate slowly at room temperature in the glove-box. After five days colorless crystals of **4** were isolated (0.055 g, 68 %). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 8.63 (d, $^3J$(H,H) = 8 Hz, 1H; Tol), 7.41–7.38 (m, 1H; Tol), 7.17 (d, $^3J$(H,H) = 8 Hz, 2H; Tol), 3.63 (s, 3H; CH$_3$ Tol), 2.55 (m, 6H; Cy), 2.17 (m, 6H; Cy), 1.78 (m, 6H; Cy), 1.70–1.50 (m, 30H; Cy) 1.25–1.15 ppm (m, 18H; Cy); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 146.5 (s; Tol), 144.1 (br s; *ipso*-C, Tol), 138.8 (s; Tol), 132.1 (s; Tol), 131.0 (s; Tol), 124.8 (s; Tol), 35.7 (vt, N = 25 Hz; C$_1$, Cy), 31.0 (br s; C$_{3,5}$, Cy), 29.8 (br s; C$_{3,5}$, Cy), 27.9 (vt, *N* = 12 Hz; C$_{2,6}$, Cy), 27.5 (overlapping vt and s; C$_{2,6}$, Cy and C$_6$H$_4$-*CH$_3$*), 26.8 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 73 ppm (s, $\omega_{1/2}$ ≈ 1620 Hz); $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 18.7 ppm (s, $^1J$(P,Pt) = 2908 Hz); elemental analysis calcd (%) for C$_{45}$H$_{77}$BBr$_2$P$_2$Pt·C$_6$H$_6$: C 54.50, H 7.44; found: C 54.38, H 7.07.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)*t*Bu}] (5)**: [Pt(PCy$_3$)$_2$] (0.060 g, 0.079 mmol) was dissolved in toluene (0.6 mL), and Br$_2$B(*t*Bu) (0.020 g, 0.088 mmol) was added to the solution. The mixture turned slightly yellow immediately. After addition of hexane (1 mL) the mixture was stored at −30 °C. After four days colorless crystals of **5** were isolated (0.051 g, 66 %). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 23 °C): $\delta$ = 2.66 (m, 6H; Cy), 2.23–2.07 (m, 12H; Cy), 1.82–1.66 (m, 30H; Cy), 1.32–1.21 (m, 18H; Cy), 1.23 ppm (s, 9H; *t*Bu); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 24 °C): $\delta$ = 38.6 (br s; *C*Me$_3$), 37.2 (vt, N = 26 Hz; C$_1$, Cy), 31.0 (s; C$_{3,5}$, Cy), 30.9 (s; C$_{3,5}$, Cy), 30.7 (s; C*Me*$_3$), 27.9 (2 overlapping vt, *N* = 10 Hz; C$_{2,6}$, Cy), 26.7 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, CD$_2$Cl$_2$, 23 °C): $\delta$ = 80 ppm (s, $\omega_{1/2}$ ≈ 1980 Hz); $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$, 24 °C): $\delta$ = 23.7 ppm (s, $^1J$(P,Pt) = 2962 Hz); elemental analysis calcd (%) for C$_{40}$H$_{75}$BBr$_2$P$_2$Pt·0.5(C$_7$H$_8$): C 50.74, H 7.73; found: C 50.71, H 7.70.

***trans*-[(Cy$_3$P)$_2$Pt(Br)(BBr$_2$)] (6)**: [Pt(PCy$_3$)$_2$] (0.098 g, 0.130 mmol) was dissolved in toluene in a Schlenk flask (10 mL) and cooled to −60 °C. A solution of BBr$_3$ in toluene (0.130 mmol) was added. The mixture was stirred for 1 h at −60 °C, then allowed to warm up to room temperature. After evaporation of the solvent, the residue was extracted in benzene. The filtrate was evaporated to dryness to yield **6** as a white solid, which was washed with hexane (6 mL) and dried in vacuo (0.080 g, 61 %). Crystals suitable for X-ray diffraction were obtained by recrystallization from toluene/hexane. $^1$H NMR (500 MHz, C$_6$D$_6$, 23 °C): $\delta$ = 2.88 (m, 6H; Cy), 2.30–2.22 (m, 12H; Cy), 1.82–1.57 (m, 30H; Cy), 1.37–1.18 ppm (m, 18H; Cy); $^{13}$C NMR (126 MHz, C$_6$D$_6$, 23 °C): $\delta$ = 36.1 (vt, *N* = 28 Hz; C$_1$, Cy), 30.9 (s; C$_{3,5}$, Cy), 27.8 (vt, *N* = 11 Hz; C$_{2,6}$, Cy), 26.9 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 23 °C): $\delta$ = 54 ppm (signal is too broad and weak to calculate $\omega_{1/2}$); $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 23 °C): $\delta$ = 19.5 ppm (s, $^1J$(P,Pt) = 2683 Hz); elemental analysis calcd (%) for C$_{36}$H$_{66}$BBr$_3$P$_2$Pt: C 42.96, H 6.61; found: C 43.71, H 6.72.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)NMe$_2$}] (7)**: Br$_2$BNMe$_2$ (0.020 g, 0.093 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) and the resulting solution was added to solid [Pt(PCy$_3$)$_2$] (0.070 g, 0.093 mmol). After 30 min, the light yellow solution was layered with hexane (1.5 mL). The solvent was allowed to evaporate slowly. After 48 h, colorless crystals of **7** were obtained at room temperature (0.075 g, 83 %). Crystals suitable for X-ray analysis were obtained by cooling a concentrated toluene solution to −30 °C. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 21 °C): $\delta$ = 3.18 (s, 3H; NMe$_2$), 2.89 (s, 3H; NMe$_2$), 2.64 (m, 6H; Cy), 2.07 (m, 6H; Cy), 1.90–1.55 (m, 36H; Cy), 1.24 ppm (m, 18H; Cy); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 21 °C): $\delta$ = 46.6 (s; NMe$_2$), 41.2 (s; NMe$_2$), 35.3 (vt, *N* = 28 Hz; C$_1$, Cy), 30.8 (br s; C$_{3,5}$, Cy), 30.0 (br s; C$_{3,5}$, Cy), 28.2 (vt, *N* = 10 Hz; C$_{2,6}$, Cy), 28.0 (vt, N = 10 Hz; C$_{2,6}$, Cy), 27.0 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 21 °C): $\delta$ = 30 ppm (s, $\omega_{1/2}$ ≈ 950 Hz); $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$, 21 °C): $\delta$ = 23.6 ppm (s, $^1J$(P,Pt) = 2811 Hz); elemental analysis calcd (%) for C$_{38}$H$_{72}$NBBr$_2$P$_2$Pt: C 47.02, H 7.48, N 1.44; found: C 46.83, H 7.33, N 1.45.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(Br)Pip}] (8)**: Br$_2$BPip (0.011 g, 0.045 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) and the resulting solution was added to solid [Pt(PCy$_3$)$_2$] (0.034 g, 0.045 mmol). After 30 min, the light yellow solution was layered with hexane. The solvent was then allowed to evaporate slowly. After 48 h, colorless crystals of **8** were isolated (0.032 g, 71 %). $^1$H NMR (500 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 4.02 (m, 2H; NC$_5$H$_{10}$), 3.67 (m, 2H; NC$_5$H$_{10}$), 3.00 (m, 6H; Cy), 2.34 (m, 6H; Cy), 2.18 (m, 6H; Cy), 1.78 (m, 24H; Cy), 1.66 (m, 6H; Cy), 1.58 (m, 2H; NC$_5$H$_{10}$), 1.48 (m, 2H; NC$_5$H$_{10}$), 1.43 (m, 2H; NC$_5$H$_{10}$), 1.40–1.20 ppm (m, 18H; Cy); $^{13}$C NMR (126 MHz, C$_6$D$_6$, 25 °C): $\delta$ = 55.5 (s; C$_2$, NC$_5$H$_{10}$), 50.8 (s; C$_6$, NC$_5$H$_{10}$), 35.9 (vt, *N* = 26 Hz; C$_1$, Cy), 31.0 (br s; C$_{3,5}$, Cy), 30.4 (br s; C$_{3,5}$, Cy), 28.3 (vt, *N* = 10 Hz; C$_{2,6}$, Cy), 28.1 (vt, *N* = 11 Hz; C$_{2,6}$, Cy), 27.1 (s; C$_4$, Cy), 26.5 (s; C$_5$, NC$_5$H$_{10}$), 26.0 (s; C$_3$, NC$_5$H$_{10}$), 25.6 ppm (s; C$_4$, NC$_5$H$_{10}$); $^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 26 °C): $\delta$ ≈ 32 ppm (s, $\omega_{1/2}$ ≈ 800 Hz); $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 25 °C): $\delta$ = 24.6 ppm (s, $^1J$(P,Pt) = 2867 Hz); elemental analysis calcd (%) for C$_{41}$H$_{76}$NBBr$_2$P$_2$Pt: C 48.72, H 7.58, N 1.39; found: C 48.71, H 7.49, N 1.51.

***trans*-[(Cy$_3$P)$_2$Pt(Br)(BCat)] (9)**: BrBCat (0.013 g, 0.066 mmol) and [Pt(PCy$_3$)$_2$] (0.050 g, 0.066 mmol) were dissolved in toluene (0.5 mL). A fine white precipitate immediately formed. The mixture was layered with hexane (2.0 mL) and stored in the glove-box until the solid had settled down. After 24 h the supernatant solution was removed and the remaining solid was washed with hexane (3 × 2.0 mL). The residual solvent was allowed to evaporate in the glove-box. Compound **9** was then isolated as a white solid (0.047 g, 75 %). $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 21 °C): $\delta$ = 7.11–7.09 (m, 2H; Cat), 6.95–6.93 (m, 2H; Cat), 2.29 (m, 6H; Cy), 2.10–0.90 ppm (m, 60H; Cy); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$ , 22 °C): $\delta$ = 149.7 (s; Cat), 121.4 (s; Cat), 111.5 (s; Cat), 36.0 (vt, *N* = 29 Hz; C$_1$, Cy), 30.2 (s; C$_{3,5}$, Cy), 27.9 (vt, *N* = 10 Hz; C$_{2,6}$, Cy), 26.8 ppm (s; C$_4$, Cy); $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$, 21 °C): $\delta$ = 28.7 ppm (s, $^1J$(P,Pt) = 2587 Hz). Owing to the poor solubility of the compound, no resonance could be observed in the $^{11}$B{$^1$H} NMR spectrum; elemental analysis for calcd (%) for C$_{36}$H$_{66}$BBrP$_2$PtO$_2$: C 52.84, H 7.39; found: C 52.73, H 7.33.

***trans*-[(Cy$_3$P)$_2$Pt(Br)(BCat′)] (10)**: BrBCat′ (0.0180 g, 0.079 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) and added to solid [Pt(PCy$_3$)$_2$] (0.060 g, 0.079 mmol). After 30 min, the light yellow solution was layered with hexane. The solvent was allowed to evaporate slowly in the glove-box. After three days colorless crystals of **10** were isolated at room temperature (0.050 g, 65 %). Crystals suitable for X-ray diffraction were obtained by recrystallization from toluene/hexane. $^1$H NMR (500 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 7.39 (d, $^4J$(H,H) = 2 Hz, 1H; Cat′), 7.16 (m, 1H; Cat′), 6.92 (dd, $^3J$(H,H) = 8 Hz and $^4J$(H,H) = 2 Hz, 1H; Cat′), 2.61 (m, 6H; Cy), 2.28–2.22 (m, 12H; Cy), 1.86–1.71 (m, 24H; Cy), 1.55 (m, 6H; Cy), 1.21 (s, 9H; *t*Bu) 1.19–1.11 ppm (m, 18H; Cy); $^{13}$C NMR (126 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 150.3 (s; Cat′), 148.1 (s; Cat′), 145.2 (s; Cat′), 118.3 (s; Cat′), 110.6 (s; Cat′), 109.2 (s; Cat′), 36.3 (vt, *N* = 28 Hz; C$_1$, Cy), 34.7 (s; *C*Me$_3$), 31.8 (s; C*Me*$_3$), 30.6 (s; C$_{3,5}$, Cy), 28.0 (vt, *N* = 11 Hz; C$_{2,6}$, Cy), 27.0 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 32 ppm (signal is too broad and weak to calculate $\omega_{1/2}$); $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 25 °C): $\delta$ = 29.0 ppm (s, $^1J$(P,Pt) = 2609 Hz); elemental analysis calcd (%) for C$_{46}$H$_{78}$BbrO$_2$P$_2$Pt: C 54.66, H 7.78; found: C 54.64, H 7.22.

***trans*-[(Cy$_3$P)$_2$Pt(Br){B(NMe$_2$)$_2$}] (11)**: BrB(NMe$_2$)$_2$ (0.020 g, 0.112 mmol) was dissolved in C$_6$H$_6$ (1.0 mL) and the resulting solution was added to solid [Pt(PCy$_3$)$_2$] (0.085 g, 0.112 mmol). After seven days the pale yellow solution was layered with hexane (2.0 mL). The solvent was allowed to evaporate slowly in the glove-box. After three days colorless crystals of **11** were isolated (0.87 g, 83 %). $^1$H NMR (500 MHz, C$_6$D$_6$, 23 °C): $\delta$ = 3.17 (s, 6H; NMe$_2$), 2.78 (br s, 6H; Cy), 2.74 (s, 6H; NMe$_2$), 2.30–2.22 (m, 12H; Cy), 1.84–1.63 (m, 30H; Cy), 1.39–1.20 ppm (m, 18H; Cy); $^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 47.0 (s; NMe$_2$), 42.4 (s; NMe$_2$), 36.6 (vt, *N* = 27 Hz; C$_1$, Cy), 30.8 (br s; C$_{3,5}$, Cy), 28.2 (vt, *N* = 11 Hz; C$_{2,6}$, Cy), 27.1 ppm (s; C$_4$, Cy); $^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 28 ppm (signal is too broad and weak to calculate $\omega_{1/2}$); $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 24 °C): $\delta$ = 27.4 ppm (s, $^1J$(P,Pt) = 3067 Hz); elemental analysis calcd (%) for C$_{40}$H$_{78}$N$_2$BBrP$_2$Pt: C 51.39, H 8.41, N 3.00; found: C 51.06, H 7.98, N 2.90.

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[13] The crystallographic data of compounds **4–8**, **10**, **11** were collected on Bruker X8APEX or Apex D8 diffractometers at 100 K and at 173 K, respectively, with CCD area detectors and multi-layer mirror or graphite monochromated $Mo_{K\alpha}$ radiation, respectively. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. **4**: $C_{49}H_{79}BBr_2P_2Pt$, $M_r = 1095.78$, colorless block, $0.21 \times 0.13 \times 0.05$ mm$^3$, monoclinic space group $P2_1/c$, $a = 16.6270(4)$, $b = 17.5834(4)$, $c = 18.1451(5)$ Å, $\beta = 114.3170(10)$, $V = 4834.2(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.506$ g cm$^{-3}$, $\mu = 4.653$ mm$^{-1}$, $F(000) = 2224$, $T = 100(2)$ K, $R_1 = 0.0240$, $wR^2 = 0.0556$, 9572 independent reflections [$2\theta = 52.28°$] and 460 parameters. **5**: $C_{43.50}H_{79}BBr_2P_2Pt$, $M_r = 1029.73$, colorless block, $0.21 \times 0.33 \times 0.35$ mm$^3$, monoclinic space group $P2_1/n$, $a = 14.9185(5)$, $b = 14.8814(6)$, $c = 20.3207(8)$ Å, $\beta = 99.4470(10)°$, $V = 4450.2(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.537$ g cm$^{-3}$, $\mu = 5.049$ mm$^{-1}$, $F(000) = 2092$, $T = 100(2)$ K, $R_1 = 0.0299$, $wR^2 = 0.0729$, 8621 independent reflections [$2\theta = 52.1°$] and 506 parameters. **6**: $C_{43}H_{74}BBr_3P_2Pt$, $M_r = 1098.59$, colorless block, $0.17 \times 0.10 \times 0.05$ mm$^3$, triclinic space group $P\bar{1}$, $a = 9.5923(7)$, $b = 14.1619(11)$, $c = 17.1076(13)$ Å, $\alpha = 100.446(2)$, $\beta = 92.269(2)$, $\gamma = 91.722(2)°$, $V = 2282.0(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.599$ g cm$^{-3}$, $\mu = 5.799$ mm$^{-1}$, $F(000) = 1100$, $T = 173(2)$ K, $R_1 = 0.0479$, $wR^2 = 0.1041$, 9020 independent reflections [$2\theta = 52.22°$] and 451 parameters. **7**: $C_{52}H_{88}BBr_2NP_2Pt$, $M_r = 1154.89$, colorless bar, $0.24 \times 0.14 \times 0.13$ mm$^3$, triclinic space group $P\bar{1}$, $a = 11.5739(4)$, $b = 19.9888(8)$, $c = 23.0307(9)$ Å, $\alpha = 92.188(2)$, $\beta = 95.782(2)$, $\gamma = 99.635(2)°$, $V = 5218.0(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.470$ g cm$^{-3}$, $\mu = 4.316$ mm$^{-1}$, $F(000) = 2360$, $T = 100(2)$ K, $R_1 = 0.0277$, $wR^2 = 0.0579$, 21541 independent reflections [$2\theta = 52.96°$] and 1063 parameters. **8**: $C_{44}H_{83}BBr_2NP_2Pt$, $M_r = 1053.77$, colorless plate, $0.19 \times 0.14 \times 0.06$ mm$^3$, triclinic space group $P\bar{1}$, $a = 12.8154(9)$, $b = 13.6144(9)$, $c = 13.9034(9)$ Å, $\alpha = 100.4090(10)$, $\beta = 99.2340(10)$, $\gamma = 102.0070(10)°$, $V = 2283.7(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.532$ g cm$^{-3}$, $\mu = 4.922$ mm$^{-1}$, $F(000) = 1074$, $T = 173(2)$ K, $R_1 = 0.0354$, $wR^2 = 0.0761$, 8991 independent reflections [$2\theta = 52.16°$] and 460 parameters. **10**: $C_{53}H_{86}BBrO_2P_2Pt$, $M_r = 1102.97$, colorless block, $0.44 \times 0.34 \times 0.20$ mm$^3$, triclinic space group $P\bar{1}$, $a = 10.218(4)$, $b = 11.956(5)$, $c = 23.232(9)$ Å, $\alpha = 79.845(6)$, $\beta = 80.507(6)$, $\gamma = 67.476(6)°$, $V = 2566.0(17)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.428$ g cm$^{-3}$, $\mu = 3.613$ mm$^{-1}$, $F(000) = 1136$, $T = 173(2)$ K, $R_1 = 0.0371$, $wR^2 = 0.0884$, 10150 independent reflections [$2\theta = 52.34°$] and 542 parameters. **11**: $C_{40}H_{78}BBrN_2P_2Pt$, $M_r = 934.79$, colorless block, $0.050 \times 0.120 \times 0.170$ mm$^3$, monoclinic space group $P2_1/n$, $a = 12.3125(4)$, $b = 11.4504(3)$, $c = 29.7911(9)$ Å, $\beta = 97.0230(10)°$, $V = 4168.5(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.490$ g cm$^{-3}$, $\mu = 4.431$ cm$^{-1}$, $F(000) = 1920$, $T = 100(2)$ K, $R_1 = 0.0440$, $wR^2 = 0.0962$, 15789 independent reflections [$2\theta = 68.52°$] and 461 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-642768–CCDC-642774. 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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