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Wolfphos in Sheep's Clothing: The First Trinuclear Triboryl- and Other Boryl Platinum Complexes Featuring a Flexible Phosphine Ligand

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Dedicated to Professor Heinrich Nöth on the Occasion of His 85th Birthday

Keywords: Boron; Platinum; Complex; Boryl; Phosphine; Flexible steric bulk

Abstract. Studies on the reactivity of the novel bis(phosphine) platinum complex [Pt{P(CH_2Cy)$_3$}$_2$] towards haloboranes are presented. The resulting complexes of the general formula *trans*-[Pt{B(*R*)*R'*}*X*{P(CH_2Cy)$_3$}$_2$] were isolated in good to excellent yields (82–91 %) and the molecular structure of *trans*-[Pt{B(Br)Fc}Br{P(CH_2Cy)$_3$}$_2$] is reported. The reactions of 1,4-(Br_2B)$_2$$C_6H_4$ and 1,3,5-(Br_2B)$_3$$C_6H_3$ with two and three equivalents of the platinum precursor yield the corresponding di- and trinuclear boryl platinum complexes, respectively. The structural characterization of the first trinuclear triboryl complex 1,3,5-*trans*-[Pt(BBr)Br{P(CH_2Cy)$_3$}$_2$]$_3$$C_6H_3$ extends the number of possible structural motifs in boryl platinum chemistry by a noteworthy example and confirms that P(CH_2Cy)$_3$ has flexible steric bulk.

Introduction

The stabilization of low valent transition metal complexes without the disadvantage of lowering the reactivity by steric overcrowding of the central metal atom is a general problem in organometallic chemistry and homogeneous catalysis. Some carbene-type ligands with flexible steric bulk of the NHC type (NHC: N-heterocyclic carbenes; *Glorius* et al.) and also one of the CAAC-type [CAAC: cyclic (alkyl)(amino)carbene; *Bertrand* et al.], found applications e.g. in the activation of aryl chlorides in Suzuki cross-coupling reactions,[1] the Suzuki-Miyaura cross-coupling of sterically hindered aryl chlorides,[2] and the α-arylation of propiophenone.[3]

In order to generate an easy-to-prepare platinum complex featuring a phosphine ligand with flexible substituents at the phosphorus atoms that has both the potential to either stabilize low-valent metal complexes or free the coordination site when required, we have developed the unusual *Wolfphos* ligand P(CH_2Cy)$_3$. The corresponding platinum precursor [Pt{P(CH_2Cy)$_3$}$_2$] (**2**) can be thought of as an easy to handle and bench-stable derivative of the elusive bisphosphine platinum complex [Pt(PMe_3)$_2$].

Recently we showed that the reactivity of **2** is unprecedented in allowing for the investigation of the dehydrocoupling reaction of catBH and its mechanism.[4] A remarkable finding of this project was the likely formation of a Pt^{IV} intermediate as the key compound of the catalytic cycle of this reaction.

The oxidative addition reaction of the B–*X* bond (*X* = F, Cl, Br, I) to phosphine platinum complexes is now well investigated[5] and has proven beneficial for the synthesis of model compounds for intermediates in transition-metal-catalyzed borylation reactions.[6] A suitable platinum precursor for the isolation of boron-centered ligands, especially in unprecedented coordination modes, is [Pt(PCy_3)$_2$] (**1**, Cy = cyclohexyl)[7] because the addition of B–*X* bonds forms complexes of the general formula *trans*-[Pt{B(*R*)*R'*}*X*(PCy_3)$_2$] commonly with high selectivity.[8] Aside from the sterically crowded platinum precursor [Pt(PCy_3)$_2$], several different phosphine platinum complexes can be used as precursors for the preparation of boryl platinum complexes, e.g. [Pt(PPh_3)$_4$], [Pt(PPh_3)$_3$],[9] [Pt(P*i*Pr_3)$_3$],[10] [Pt(PEt_3)$_4$].[11] All these complexes react with dissociation of at least one phosphine ligand, which can form adducts with the Lewis-acidic haloboranes, both necessitating unwanted workup steps and lowering the yield of the goal compounds. An alternative to these [Pt(PR_3)$_{2+n}$] complexes might be [Pt(η^2-C_2H_4)(PPh_3)$_2$], but its reactivity is restricted to only a few haloboranes, e.g. ClBcat (cat = 1,2-$O_2C_6H_4$).[12] Particularly for boryl platinum complexes featuring phosphine ligands with sterically less demanding substituents, there is a lack of suitable precursors.

Herein we report the preparation and characterization of a handful of new boryl platinum complexes, among them the first representative of a triboryl complex with an aryl spacer, accessible through an oxidative addition protocol without the formation of any byproducts.

Results and Discussion

In order to generalize the reactivity of the novel platinum species [Pt{P(CH_2Cy)$_3$}$_2$] (**2**), we reacted the compound with

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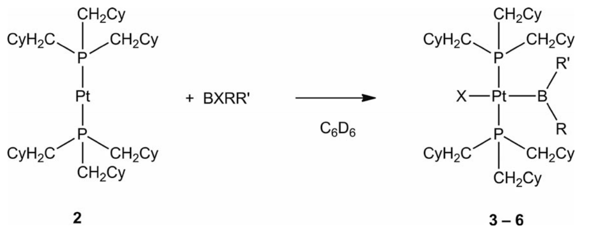
several haloboranes B*XRR*′ (*X* = *R* = Br, *R*′ = Fc, NMe_2; *X* = Br, *R* = *R*′ = NMe_2; *X* = *R* = *R*′ = I). The observation of the reactions with NMR spectroscopy reveals the quantitative formation of boryl platinum complexes of the general formula $[Pt\{B(R)(R')\}X\{P(CH_2Cy)_3\}_2]$ [*X* = *R* = Br, *R*′ = Fc (**3**), NMe_2 (**4**); *X* = Br, *R* = *R*′ = NMe_2 (**5**); *X* = *R* = *R*′ = I (**6**)] within minutes at ambient temperature, whereas the formation of **5** is complete within 2 d at 40 °C (Scheme 1). Remarkably, the reaction of **2** with BI_3 is very selective even in presence of an excess of haloborane and at elevated temperatures. The compounds **3**–**6** can be isolated as amorphous, analytically pure compounds by evaporation of the solvent.



Scheme 1. Synthesis of novel boryl complexes by B–*X*-oxidative addition (**3**: *X* = *R* = Br, *R*′ = Fc, **4**: NMe_2; **5**: *X* = Br, *R* = *R*′ = NMe_2; **6**: *X* = *R* = *R*′ = I).

The (boryl)(halogeno)platinum complexes **3**–**5** exhibit $^{31}P\{^1H\}$ NMR signals shifted about 10–20 ppm to lower frequencies (11.9–0.8 ppm) relative to the signal of **2** (δ = 23.5 ppm), whereas the signal of **6** occurs at –9.0 ppm. Both the relative chemical shift as well as the P–Pt coupling constant feature values that are similar to those of the related systems *trans*-$[Pt\{B(R)(R')\}X(PCy_3)_2]$ ($^1J_{P,Pt}$ = 2647–2959 Hz). By layering a saturated solution of **3** in benzene with hexanes, red crystals suitable for X-ray diffraction analysis could be isolated (Figure 1).

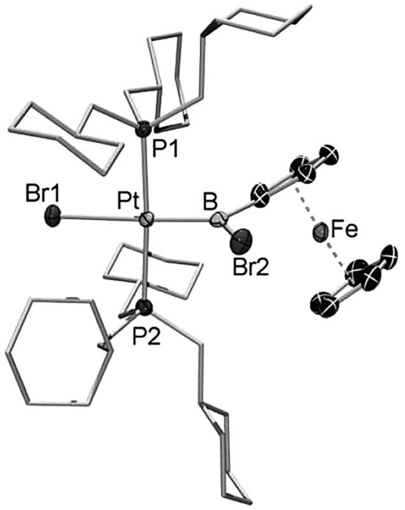
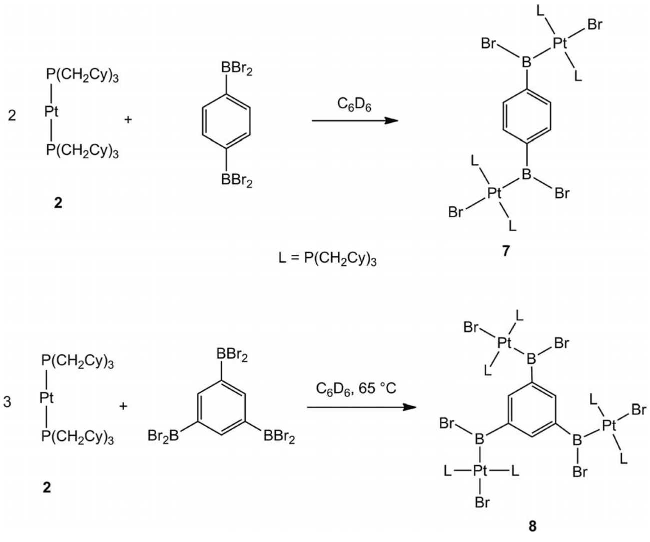


Figure 1. Molecular structure of *trans*-$[Pt\{B(Br)Fc\}Br\{P(CH_2Cy)_3\}_2]$ as derived from X-ray crystallography. Thermal ellipsoids depicted at the 50 % probability level. For clarity, hydrogen atoms and one molecule of co-crystallized benzene are removed and cyclohexyl groups are simplified. Selected bond lengths /pm and angles /°: Pt–B 198.9(4), Pt–Br1 261.15(6), P1–Pt–P2 175.95(3), B–Pt–Br1 177.3(1).

Compound **3** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure exhibits the expected, slightly distorted, square-planar *trans*-configured boryl platinum complex. The bond lengths at the central metal atom are very similar to those of *trans*-$[Pt\{B(Br)Fc\}Br(PCy_3)_2]$ and *trans*-$[Pt\{B(Br)Fc\}Br(PiPr_3)_2]$ whereas the P1–Pt–P2 angle of 177.3(1)° is the largest observed in boryl platinum complexes and is very close to the ideal 180° in a perfectly square planar arrangement. This finding might be explained by the large steric demand of the phosphine ligand that results in the maximum avoidance of the cyclohexyl groups. The phosphine substituents have an eclipsed orientation concerning the phosphine-bound methylene carbon atoms, whereas two cyclohexyl groups each point towards the vacant coordination sites at the central platinum atom. The third cyclohexyl substituent is oriented towards the boryl moiety, whereas the unrestricted rotation around the methylene carbon atom allows for the avoidance of the cyclohexyl ring and the {B(Br)Fc} group. A measure for the steric demand is given through the *percent buried volume*[13] which gives a value[14] of 28.9 %. This volume is about one quarter smaller than that of the free phosphine ligand (39.7 %) and even smaller than that of PCy_3 (31.8 %).

The strikingly selective reactivity of **2** towards highly reactive haloboranes such as BI_3 motivated us to investigate its reactivity towards dibromoboranes with aryl spacers, which are known to react unselectively with **1**. Mixing of 1,4-$C_6H_4(BBr_2)_2$ with two equivalents of **2** yields 1,4-*trans*-$[Pt(BBr)Br\{P(CH_2Cy)_3\}_2]_2(C_6H_4)$ (**7**) as a slightly yellow, moderately air sensitive solid in 74 % yield. Monitoring the reaction with NMR spectroscopy reveals the formation of a single phosphorus-containing product in the $^{31}P\{^1H\}$ NMR spectrum as a singlet signal in the expected range with platinum satellites (δ = 3.9, $^1J_{P,Pt}$ = 2750 Hz) (Scheme 2).



Scheme 2. Synthesis of di- and trinuclear boryl platinum complexes with aryl spacers.

The reaction of **2** with three equivalents of 1,3,5-$(BBr_2)_3C_6H_3$ in benzene takes 16 h at 65 °C for full transformation of the starting materials to 1,3,5-*trans*-

$[Pt(BBr)Br\{P(CH_2Cy)_3\}_2]_3C_6H_3$ (**8**) as confirmed by NMR spectroscopy. A new signal in the ^1H NMR ($\delta = 9.56$ ppm) for the aryl protons and a single ^{31}P NMR resonance at $\delta = 3.4$ ($^1J_{P,Pt} = 2745$ Hz) reveals the formation of a symmetric product.

Compound **8** crystallizes in the tetragonal space group $P4_2/n$ with two molecules in the asymmetric unit (Figure 2).

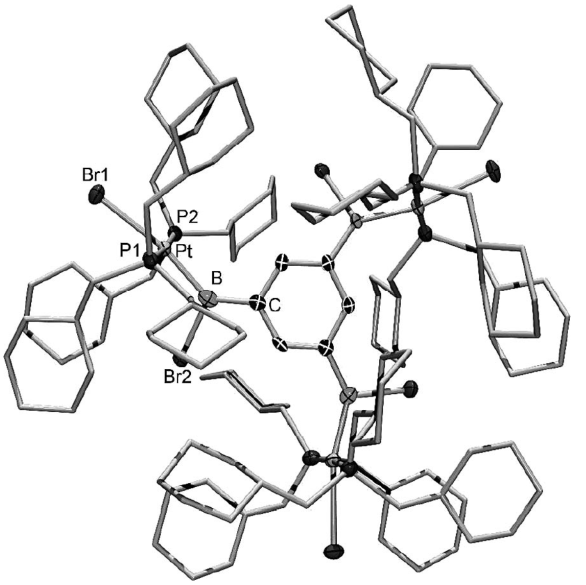


Figure 2. Molecular structure of 1,3,5-*trans*-$[Pt(BBr)Br\{P(CH_2Cy)_3\}_2]_3C_6H_3$ (**8**) as derived from X-ray crystallography. Thermal ellipsoids depicted at the 50 % probability level. For clarity, only one of two molecules in the asymmetric unit is displayed, hydrogen atoms are removed and phosphine substituents are simplified. Selected bond lengths /pm and angles /° for one exemplary platinum fragment: Pt–B 198.6(9), Pt–Br 261.94(8), Pt–P1 231.5(2), Pt–P2 232.3(2), average C–C 140.5, P1–Pt–P2 176.05(7), B–Pt–Br1 169.4(3), P1–Pt–C–C ca. 100.0.

The molecular structure confirms the formation of a symmetric, trinuclear triboryl complex with an aryl spacer, in which every platinum atom is coordinated in a square planar *trans* arrangement. The clean formation of a trinuclear boryl complex is unprecedented and corroborates the concept of *flexible steric bulk*, given that $[Pt(PCy_3)_2]$ decomposes when treated with the triborylaryl reagent due to dissociation of the more rigid phosphine, followed by phosphine-borane adduct formation.[16] Because of the structural similarities of every single central platinum atom, only one complex fragment is discussed in detail. The Pt–P axes are oriented nearly orthogonal to the plane defined by the aryl carbon atoms (P–Pt–C–C ≈100°). Similar to the arrangement in **3**, the phosphorus-bound methylene carbon atoms are eclipsed, whereas two cyclohexyl rings are each oriented towards the free coordination site at the platinum atom. The third cyclohexyl ring at each phosphine is situated above the metal–boron bond and adopts an umbrella-like position, shielding and kinetically stabilizing the Pt–B bond. The average C–C distance in the central phenyl ring (140.5 pm) lies in the typical range of that in benzene. The bonding distances and angles at the platinum center lie in the expected range for platinum boryl complexes [Pt–B 198.6(9) pm, Pt–Br 261.94(8) pm, Pt–P1 231.5(2) pm, Pt–P2 232.3(2) pm, P1–Pt–P2 176.05(7)°, B–Pt–Br 169.4(3)°]. It should be noted that compound **8** represents the first trinuclear triboryl complex.

Conclusions

Reactivity studies of the novel bis(phosphine) platinum complex $[Pt\{P(CH_2Cy)_3\}_2]$ (**2**) towards haloboranes disclose a strikingly selective reactivity of **2**. The resulting complexes *trans*-$[Pt\{B(R)R'\}X\{P(CH_2Cy)_3\}_2]$ [$X = R =$ Br, $R' =$ Fc (**3**), NMe_2 (**4**); $X =$ Br, $R = R' = NMe_2$ (**5**); $X = R = R' =$ I (**6**)] were isolated in higher yields (82–91 %) than their PCy_3 derivatives throughout, whereas the investigation of the molecular structure of **3** indicated structural similarities of the respective PCy_3 systems. Whereas the high yield of the dinuclear complex 1,4-*trans*-$[Pt(BBr)Br\{P(CH_2Cy)_3\}_2]_2(C_6H_4)$ (**7**) compared to that of the PCy_3-substituted dinuclear complex again corroborates the selective reactivity, the formation and structural characterization of the first trinuclear triboryl complex 1,3,5-*trans*-$[Pt(BBr)Br\{P(CH_2Cy)_3\}_2]_3C_6H_3$ (**8**) extends the number of possible structural motifs in boryl platinum chemistry by a noteworthy example and confirms that the $P(CH_2Cy)_3$ ligand has flexible steric bulk.

Experimental Section

All manipulations were conducted either in an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. BBr_2Fc,[17] BBr_2NMe_2,[18] $BBr(NMe_2)_2$,[18] BI_3,[19] 1,4-$(Br_2B)_2C_6H_4$, and 1,3,5-$(Br_2B)_3C_6H_3$[20] were prepared according to published procedures. Solvents were dried according to standard procedures, degassed, and stored in an argon atmosphere over activated molecular sieves. C_6D_6 was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. Reagents were dried and purified by standard procedures. NMR spectra were acquired with a Bruker AMX 400 or a Bruker Avance 500 NMR spectrometer. Chemical shifts are given in ppm and are referenced against external Me_4Si (^1H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B), and H_3PO_4 (85 %, ^{31}P). Assignments were made from the analysis of ^1H,^{13}C-HMQC, and ^1H,^{13}C-HMBC NMR spectroscopic experiments. Microanalyses (C, H, N) were performed with a Leco Instruments elemental analyzer, type CHNS 932.

X-ray Crystallography: The crystal data of **3** were collected with a Bruker APEX diffractometer with a CCD area detector and graphite monochromated Mo-K_α radiation, those of **8** were collected with a Bruker SMART-APEX diffractometer with a CCD area detector and multi-layer mirror monochromated Mo-K_α radiation. The structures were solved by direct methods, refined with the SHELX software package (G. Sheldrick, *Acta Crystallogr. Sect. A*, **2008**, *64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions.

The unit cell of **8** contains benzene and hexane molecules, which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

Crystal Data for 3: $C_{55}H_{90}BBr_2FeP_2Pt$, $M_r = 1234.78$, red block, $0.15 \times 0.12 \times 0.10$ mm^3, monoclinic space group $P2_1/c$, a =

14.785(5) Å, b = 16.227(4) Å, c = 23.083(6) Å, β = 105.610(7)°, V = 5334(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.538 g·cm^{-3}, μ = 4.485 mm^{-1}, F(000) = 2516, T = 174(2) K, R_1 = 0.0437, wR_2 = 0.0688, 13237 independent reflections [2θ ≤ 5664°] and 559 parameters.

Crystal Data for 8: C$_{132}$H$_{237}$B$_3$Br$_6$P$_6$Pt$_3$, M_r = 3107.20, colorless block, 0.385 × 0.294 × 0.172 mm^3, tetragonal space group $P42/n$, a = 41.7816(16) Å, b = 41.7816(16) Å, c = 18.0650(15) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 31536(3) Å^3, Z = 8, $\rho_{calcd.}$ = 1.309 g·cm^{-3}, μ = 4.276 mm^{-1}, F(000) = 12624, T = 102(2) K, R_1 = 0.0852, wR_2 = 0.1235, 29931 independent reflections [2θ ≤ 51.36°] and 1403 parameters.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-916114 (**3**) and CCDC-916113 (**8**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

***trans*-[Pt{B(Br)Fc}Br{P(CH$_2$Cy)$_3$}$_2$] (3):** A yellow solution of [Pt{P(CH$_2$Cy)$_3$}$_2$] (100 mg, 119 µmol) in C$_6$D$_6$ (0.5 mL) was mixed with BBr$_2$Fc (42.3 mg, 119 µmol). The solvent of the red reaction mixture was allowed to evaporate, yielding *trans*-[Pt{B(Br)Fc}Br{P(CH$_2$Cy)$_3$}$_2$] as a red, crystalline solid (116 mg, 82 %). Elemental analysis (calculated for C$_{52}$H$_{87}$BBr$_2$FeP$_2$Pt·C$_6$H$_6$): C 54.69 (54.77); H 7.36 (7.58) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 296 K): δ = 4.71 (br. vt, 2 H, C$_5$H$_4$B), 4.34 (br. vt, 2 H, C$_5$H$_4$B), 4.24 (br. s, 5 H, C$_5$H$_5$), 2.29–2.18 (m, 6 H, C*H*$_2$Cy), 2.14–1.10 (vbr. m, 66 H, Cy). **^{11}B{^{1}H} NMR** (128.4 MHz, C$_6$D$_6$, 294 K): δ = 82.0. **^{13}C{^{1}H} NMR** (100.6 MHz, C$_6$D$_6$, 296 K): δ = 76.3, 71.9 ([(η^5-C$_5$H$_5$)Fe(η^5-*C*$_5$H$_4$)]), 69.9 ([(η^5-*C*$_5$H$_5$)Fe(η^5-C$_5$H$_4$)]), 40.8 (br. s, CH$_2$Cy), 35.8 (*vt*, N = $|^2J_{P,C} + {}^4J_{P,C}|$ = 3 Hz), 34.9 (s, CH$_2$Cy), 33.6 (*vt*, N = $|^1J_{P,C} + {}^3J_{P,C}|$ = 16 Hz), 26.8 (s, CH$_2$Cy), 26.4 (s, CH$_2$Cy). **^{31}P{^{1}H} NMR** (400.1 MHz, C$_7$D$_8$, 296 K): δ = 4.0 ($^1J_{P,Pt}$ = 2807 Hz).

***trans*-[Pt{B(Br)NMe$_2$}Br{P(CH$_2$Cy)$_3$}$_2$] (4):** A yellow solution of [Pt{P(CH$_2$Cy)$_3$}$_2$] (20.0 mg, 24 µmol) was mixed with BBr$_2$(NMe$_2$) (5.11 mg, 23.8 µmol), leading to a colorless reaction mixture. Evaporation of the solvent yielded **4** as a colorless, amorphous solid (22.8 mg, 91 %). Elemental analysis (calculated for C$_{44}$H$_{84}$BBr$_2$NP$_2$Pt): C 50.58 (50.10); H 7.67 (8.03); N 1.09 (1.33) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 297 K): δ = 3.12 (s, 3 H, NMe$_2$), 2.98 (s, 3 H, NMe$_2$), 2.26–2.21 (m, 6 H, CH$_2$Cy), 2.08–1.97 (m, 24 H, CH$_2$Cy), 1.77–1.61 (m, 18 H, CH$_2$Cy), 1.43–1.34 (m, 12 H, CH$_2$Cy), 1.24–1.09 (m, 18 H, CH$_2$Cy). **^{11}B NMR** (128.4 MHz, C$_6$D$_6$, 298 K): δ = 36.4. **^{13}C{^{1}H} NMR** (100.6 MHz, C$_6$D$_6$, 296 K): δ = 45.0 (s, NMe$_2$), 40.8 (s, NMe$_2$), 35.9 (m, CH$_2$Cy), 34.6 (m, CH$_2$Cy), 33.7 (m, CH$_2$Cy), 26.7 (m, CH$_2$Cy), 26.5 (s, CH$_2$Cy). **^{31}P{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 298 K): δ = 6.7 ($^1J_{P,Pt}$ = 2750 Hz).

***trans*-[Pt{B(NMe$_2$)$_2$}Br{P(CH$_2$Cy)$_3$}$_2$] (5):** [Pt{P(CH$_2$Cy)$_3$}$_2$] (20 mg, 24 µmol) and BBr(NMe$_2$)$_2$ (4.3 mg, 24 µmol) were incorporated in C$_6$D$_6$ (0.5 mL) yielding a colorless reaction mixture. After 2 d at 60 °C the reaction was judged complete with NMR spectroscopy. By evaporation of the solvent in high vacuum and gentle washing of the remaining solid with hexanes, *trans*-[Pt{B(NMe$_2$)$_2$}-Br{P(CH$_2$Cy)$_3$}$_2$] was isolated as a spectroscopically pure, colorless solid (21.4 mg, 88 %). Elemental analysis (calculated for C$_{46}$H$_{90}$BBrN$_2$P$_2$Pt): C 53.93 (54.22); H 8.60 (8.90); N 2.35 (2.75) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 296 K): δ = 2.93 (s, 12 H, NMe$_2$), 2.09–2.01 (br. m, 30 H, CH$_2$Cy), 1.76–1.71 (br. m, 12 H, CH$_2$Cy), 1.65–1.61 (br. m, 6 H, CH$_2$Cy), 1.43–1.34 (br. m, 12 H, CH$_2$Cy), 1.23–1.10 (br. m, 18 H, CH$_2$Cy). **^{11}B NMR** (128.4 MHz, C$_6$D$_6$, 294 K): δ = 35.0 (FWHM ca. 1100 Hz). **^{13}C{^{1}H} NMR** (100.6 MHz, C$_6$D$_6$, 296 K): δ = 43.0 (vbr. s, NMe$_2$, *C*H$_2$Cy), 36.3 (s, Cy), 34.8 (*vt*, N = $|^1J_{P,C} + {}^3J_{P,C}|$ = 15 Hz), 26.7 (s, Cy), 26.5 (s, Cy). **^{31}P{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 294 K): δ = 11.8 (s, $^1J_{P,Pt}$ = 2960 Hz).

***trans*-[Pt(BI$_2$)I{P(CH$_2$Cy)$_3$}$_2$] (6):** To a yellow solution of [Pt{P(CH$_2$Cy)$_3$}$_2$] (20.0 mg, 23.8 µmol) in C$_6$D$_6$ (0.5 mL) colorless, solid BI$_3$ (9.4 mg, 24 µmol) was added. The reaction mixture decolored immediately. By evaporation of the solvent in high vacuum *trans*-[Pt(BI$_2$)I{P(CH$_2$Cy)$_3$}$_2$] was isolated as a colorless solid (25 mg, 84 %). Elemental analysis (calculated for C$_{42}$H$_{78}$BI$_3$P$_2$Pt): C 40.49 (40.96); H 5.99 (6.38) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 294 K): δ - = 2.34–2.30 (br. s, 12 H, CH$_2$Cy), 2.12–2.04 (m, 12 H, CH$_2$Cy), 2.02–1.90 (m, 6 H, CH$_2$Cy), 1.88–1.70 (m, 12 H, CH$_2$Cy), 1.67–1.57 (m, 6 H, CH$_2$Cy), 1.48–1.29 (m, 12 H, CH$_2$Cy), 1.24–1.08 (m, 18 H, CH$_2$Cy). **^{11}B NMR** (128.4 MHz, C$_6$D$_6$, 297.7 K): δ = 37.0. **^{13}C{^{1}H} NMR** (100.6 MHz, C$_6$D$_6$, 296 K): δ = 35.5 (m, CH$_2$Cy), 34.8 (s, CH$_2$Cy), 33.5 (m, CH$_2$Cy), 26.6 (s, CH$_2$Cy), 26.3 (m, CH$_2$Cy). **^{31}P{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 298 K): δ = –8.7 ($^1J_{P,Pt}$ = 2668 Hz).

1,4-*trans*-[Pt(BBr)Br{P(CH$_2$Cy)$_3$}$_2$]$_2$(C$_6$H$_4$) (7): [Pt{P(CH$_2$Cy)$_3$}$_2$] (20 mg, 24 µmol) and 1,4-C$_6$H$_4$(BBr$_2$)$_2$ (3.5 mg, 8.1 µmol) are diluted in C$_6$D$_6$. After 1 h, the solvent of the reaction mixture is evaporated off yielding 1,4-*trans*-[Pt(BBr)Br{P(CH$_2$Cy)$_3$}$_2$]$_2$(C$_6$H$_4$) as a moderately air-sensitive, colorless solid (17 mg, 74 %). Elemental analysis (calculated for C$_{92}$H$_{162}$B$_2$Br$_4$P$_2$Pt): C 51.49 (52.03); H 7.36 (7.69) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 296 K): δ = 8.72 (s, 4 H, C$_6$H$_4$), 2.20–1.05 (vbr. m, 156 H, Cy). **^{11}B NMR** (128.4 MHz, C$_6$D$_6$, 296 K): due to unresolved coupling to ^{31}P and ^{195}Pt nuclei, no signal can be detected. **^{13}C{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 296 K): δ = 137.33 (br. s, C$_6$H$_4$), 36.8–35.0 (m, CH$_2$Cy), 34.0 (m, CH$_2$Cy), 27.1–26.4 (m, CH$_2$Cy). **^{31}P{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 296 K): δ = 3.9, $^1J_{P,Pt}$ = 2750 Hz.

1,3,5-*trans*-[Pt(BBr)Br{P(CH$_2$Cy)$_3$}$_2$]$_3$(C$_6$H$_3$) (8): Yellow [Pt{P(CH$_2$Cy)$_3$}$_2$] (70 mg, 83 µmol) and brown 1,3,5-(Br$_2$B)$_3$C$_6$H$_3$ (16 mg, 27 µmol) were mixed in C$_6$D$_6$ (0.5 mL) and heated to 65 °C for 16 h. Evaporation of the solvent and gentle washing of the light brown residue with cold hexanes (0.5 mL) yielded 1,3,5-*trans*-[Pt(BBr)Br{P(CH$_2$Cy)$_3$}$_2$]$_3$(C$_6$H$_3$) as a colorless, crystalline solid (55 mg, 64 %). Elemental analysis (calculated for C$_{132}$H$_{237}$B$_3$Br$_6$P$_6$Pt$_3$): C 51.21 (51.02); H 7.61 (7.69) %. **^{1}H NMR** (400.1 MHz, C$_6$D$_6$, 296 K): δ = 9.56 (s, 3 H, C$_6$H$_3$), 2.34–2.05 (m, 90 H, CH$_2$Cy), 1.87–1.83 (m, 36 H, CH$_2$Cy), 1.74–1.70 (m, 18 H, CH$_2$Cy), 1.54–1.51 (m, 36 H, CH$_2$Cy), 1.30–1.17 (m, 54 H, CH$_2$Cy). **^{11}B NMR** (128.4 MHz, C$_6$D$_6$, 296 K): δ = due to unresolved coupling to ^{31}P and ^{195}Pt nuclei, no signal can be detected. **^{13}C{^{1}H} NMR** (100.6 MHz, C$_6$D$_6$, 296 K): δ = 152.1 (s, C$_6$H$_3$), the boron-bound carbon atom resonance could not be detected due to unresolved coupling; 36.3 (s, CH$_2$Cy), 34.9 (s, CH$_2$Cy), 34.6 (s, CH$_2$Cy), 34.4 (s, CH$_2$Cy), 34.3 (s, CH$_2$Cy), 26.8 (s, CH$_2$Cy), 25.5 (s, CH$_2$Cy). **^{31}P{^{1}H} NMR** (162.0 MHz, C$_6$D$_6$, 296 K): δ = 3.4 ($^1J_{P,Pt}$ = 2745 Hz).

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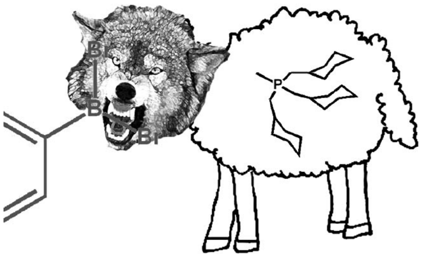
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