Conversion of *trans*-Bromoboryl Platinum Complexes into their *cis*-Analogues upon Treatment with Chelating Bisphosphines

Holger Braunschweig,* Ralph Leech, Daniela Rais, Krzysztof Radacki, and Katharina Uttinger

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

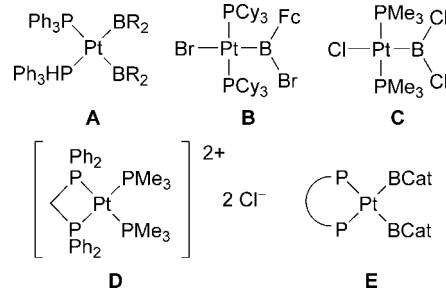
Received October 1, 2007

Oxidative addition of B−halogen bonds to Pt(0) centers generally leads to corresponding *trans*-halo(boryl)complexes. Here, we report on a series of unprecedented *cis*-bromo(boryl)species of the type *cis*-[(dcpe)Pt{B(Br)R)(Br)], which were obtained from corresponding complexes *trans*-[$(Cy_3P)_2$Pt{B(Br)R}(Br)] (R = Fc, Pip, Mes) (Cy = cyclohexyl; Fc = ferroceny; Pip = piperidyl, Mes = mesityl) upon treatment with the chelating bisphosphine dcpe (=bis(dicyclohexyl)phosphinoethane). In CH_2Cl_2 solution and in the presence of PCy_3, one of these products, *cis*-[(dcpe)Pt{B(Br)Mes)(Br)], is converted into the corresponding chloroboryl complex *cis*-[(dcpe)Pt{B(Cl)Mes)(Br)]. All compounds were fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray analyses.

Introduction

Boryl complexes of platinum play an important role as key intermediates in the catalyzed diboration of alkynes, alkenes, and other unsaturated organic compounds,[1] as well as in the C−H activation of organic substrates,[2] and have thus attracted considerable attention.[3] It has been shown that in square-planar complexes of the type $[MR_2P_2]$ (M = Ni, Pd, Pt, P = phosphine) the reductive elimination of R_2, which is a crucial step in the aforementioned catalytic cycles, is facilitated by the mutual *cis*-arrangement of the two ligands R.[4] A corresponding *trans*-disposition, however, usually precludes the reductive elimination of R_2 or requires at least much harsher conditions.[4c] Therefore, *cis*-complexes should be advantageous for possible applications in homogeneous catalysis. The oxidative addition of B−H, B−B, and B−E (E = main group element) bonds to low-valent transition metals is a commonly used method for the synthesis of boryl complexes. In the case of reactions of B−B, B−Si, or B−Sn bonds with Pt(0) species a *cis*-disposition is achieved, for example in complexes *cis*-[$(Ph_3P)_2$Pt$(BR_2)_2$] (**A**; R_2 = Cat (=1,2-O_2-C_6H_4), Pin (=2,3-O_2-2,3-Me_2-C_4H_6), F_2, (Cl, NMe_2)),[4a,5] *cis*-[$(Ph_3P)_2$Pt(BNMe_2)E] (E = $SnMe_3$, $GeMe_3$),[6] or *cis*-[$(R_3P)_2$-Pt(BPin)($SiMe_2$Ph)] (R_3 = Me_3, Me_2Ph, Et_3)[7] (Chart 1).

Chart 1. Different Types of Pt Complexes



The oxidative addition of boron−halogen (halogen = Cl, Br, I) bonds to zerovalent platinum species, however,

* Corresponding author. E-mail: h.braunschweig@mail.uni-wuerzburg.de. Fax: (+49)931-888-4623. Tel: (+49)931-888-5260.

(1) (a) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957–5026. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179–1191. (c) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695–4712. (d) Fu, G. C.; Evans, D. A.; Muci, A. R. *Adv.Catal. Processes* **1995**, *1*, 95–121. (e) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2000**, *611*, 392–402. (f) Ishiyama, T.; Miyaura, N. *Chem. Rec.* **2004**, *3*, 271–280. (g) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63–73. (h) Braunschweig, H.; Kupfer, T.; Lutz, M.; Radacki, K.; Seeler, F.; Sigritz, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4048–4051.

(2) (a) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R. *Science* **2002**, *295*, 305–308. (b) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172–2174. (c) Ishiyama, T.; Nobuta, Y.; Hartwig, J. F.; Miyaura, N. *Chem. Commun.* **2003**, 2924–2925. (d) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3–11. (e) Ishiyama, T.; Miyaura, N. *Pure Appl. Chem.* **2006**, *78*, 1369–1375. (f) Mkhalid, I. A. I.; Conventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N.; Marder, T. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 489–491. (g) Murphy, J. M.; Lawrence, J. D.; Kawamura, K.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 13684–13685.

(3) (a) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535–559. (b) Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786–1801. (c) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254–5274. (d) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685–2722. (e) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1–51.

(4) (a) Clegg, W.; Lawlor, F. J.; Lesley, G.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Scott, A. J.; Souza, F. E. S. *J. Organomet. Chem.* **1998**, *550*, 183–192. (b) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466–1468. (c) Crabtree Robert, H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons, Inc: Hoboken, NJ, 2005; 4th ed., pp 173–174.

(5) (a) Curtis, D.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1687–1694. (b) Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 4403–4404. (c) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137–5154. (d) Lu, N.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Timms, P. L.; Whittell, G. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4032–4037. (e) Kerr, A.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Quayle, M. J.; Rice, C. R.; Timms, P. L.; Whittell, G. R. *Chem. Commun.* **1998**, 319–320. (f) Iverson, C. N.; Smith, M. R. *Organometallics* **1996**, *15*, 5155–5165. (g) Ishiyama, T.; Matsuda, N.; Murata, M; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713–720. (h) Clegg, W.; Johann, T. R. F.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Peakman, T. M.; Quayle, M. J.; Rice, C. R.; Scott, A. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1431–1438.

(6) Habereder, T.; Noeth, H. *Appl. Organomet. Chem.* **2003**, *17*, 525–538.

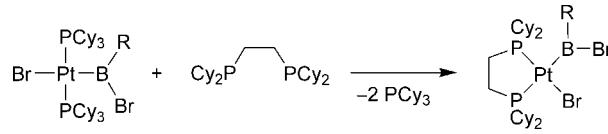
(7) Sagawa, T.; Asano, Y.; Ozawa, F. *Organometallics* **2002**, *21*, 5879–5886.

10.1021/om700976t CCC: $40.75
Publication on Web 01/16/2008

generally leads to corresponding *trans*-platinum(halo)boryls, e.g., *trans*-[$(R_3P)_2Pt(BCl_2)(Cl)$] (R_3 = Me_3, Me_2Ph, $MePh_2$, Ph_3),[8] *trans*-[$(Ph_3P)_2Pt(BR_2)(Cl)$] (R_2 = Cat, (Cl, NMe_2)),[4a,5a] *trans*-[$(Cy_3P)_2Pt${B(Br)Fc}(Br)] (**B**; Cy = cyclohexyl; Fc = ferrocenyl),[9] and *trans*-[$(Cy_3P)_2Pt(BI_2)(I)$].[10] Recent computational[11] and experimental[12] studies on these systems have proven the R_2B ligand to exert an exceptionally strong *trans*-influence. Moreover, the oxidative addition of B−Br bonds in particular allowed for the realization of novel Pd and Pt complexes with boron-centered ligands in highly unusal coordination modes including heterodinuclear[13] and cationic borylene complexes,[12a,14] base-stabilized borylenes,[15] bridging boryl complexes,[16] and iminoboryl complexes.[17]

In continuation of our work in this area, we wondered if corresponding *cis*-halo(boryl) complexes were accessible, employing chelating bisphosphine ligands. Access to these target compounds may be achieved by (i) oxidative addition of haloboranes to zerovalent species [(PP)PtL] (PP = bisphosphine, L = labile ligand) or (ii) subsequent conversion of divalent complexes *trans*-[$(R_3P)_2Pt(BR_2)(Hal)$] upon reaction with suitable bisphosphines PP. For the higher homologues of B, i.e., Al, Ga, and In, the former method was successfully applied to the synthesis of complexes of the type *cis*-[(dcpe)Pt(ER_2)(R)] (dcpe = bis(dicyclohexylphosphino)ethane; E = Al, Ga, In; R = CH_2CMe_3, CH_2SiMe_3).[18] However, attempts to exchange the phosphines in *trans*-[$(Me_3P)_2Pt(BCl_2)(Cl)$] (**C**) with dppm (=bis(diphenylphosphino)methane) led to cleavage of the Pt−B bond and formation of *cis*-[$(Me_3P)_2Pt$(dppm)]Cl_2 (**D**),[5a] although similar *trans–cis* conversions were successfully achieved with different sets of Pt-bound ligands (e.g., [(PP)Pt(Cl)CF_3], [(dppe)-Pt(Cl)(2-C_5H_4N)]; dppe = bis(diphenylphosphino)ethane).[19] Moreover, it was shown that the two monodentate phosphines in complexes of the type *cis*-[$(Ph_3P)_2Pt(BR_2)_2$] (**A**) can be easily exchanged by a chelating bisphosphine with retention of the *cis*-geometry, yielding, for example, *cis*-[(PP)Pt$(BCat)_2$] (**E**).[5d]

Scheme 1. Conversion of *trans*-Bromoboryl Complexes into their *cis*-Analogues by Addition of dcpe[a]



[a] (a) R = Fc; C_6H_6, RT; **1** → **2**; (b) R = Pip; Tol, 80 °C; **3** → **4**; (c) R = Mes; C_6H_6, 45 °C; **5** → **6**.

In the present paper we report on the reactivity of *trans*-bromo(boryl) complexes of platinum toward chelating bisphosphines, thus establishing a fully characterized series of unprecedented *cis*-bromo(boryl) species.

Results and Discussion

Synthesis and NMR Spectroscopic Characteristics. The reaction of the platinum boryl complex *trans*-[$(Cy_3P)_2$-Pt{B(Br)Fc}(Br)] (**1**) with dcpe was investigated by means of multinuclear NMR spectroscopy. After 6 h the consumption of the starting materials of the 1:1 mixture, formation of free PCy_3, and the appearance of two new signals could be observed in the $^{31}P\{^1H\}$ NMR spectrum. These spectroscopic findings indicate the exchange of PCy_3 by the chelating bisphosphine and the conversion of the *trans*-boryl complex **1** into a related *cis*-species, with different chemical environments for the two phosphorus nuclei (Scheme 1). Compared to the starting boryl complex (δ (^{31}P) = 21.5 ppm; $^1J_{P\text{-}Pt}$ = 2892 Hz)[9] the two signals are downfield shifted, and the broad resonance at 65.0 ppm ($^1J_{P\text{-}Pt}$ = 1098 Hz) can be assigned to the phosphorus atom in *trans*-position to the boron center, while the sharp peak at 52.0 ppm ($^1J_{P\text{-}Pt}$ = 4140 Hz) arises from the phosphorus atom *trans* to bromide. The new compound was isolated in 71% yield as an orange solid, and single crystals suitable for X-ray diffraction analysis, which confirmed the expected constitution of *cis*-[(dcpe)Pt{B(Br)Fc)(Br)] (**2**) (*vide infra*, Figure 1), could be obtained by slow evaporation of a toluene solution of the reaction mixture.

In contrast to the formation of **2**, the corresponding reaction of the aminoboryl species *trans*-[$(Cy_3P)_2Pt${B(Br)Pip}(Br)] (**3**) with dcpe in toluene is much slower, and heating at 80 °C for 7 days is required to reach completion of the phosphine exchange with concomitant *trans–cis* rearrangement. In the $^{31}P\{^1H\}$ NMR spectrum a broad signal at 65.3 ppm ($^1J_{P\text{-}Pt}$ = 1187 Hz) and a sharp one at 53.5 ppm ($^1J_{P\text{-}Pt}$ = 4108 Hz) can be detected. The boryl complex *cis*-[(dcpe)Pt{B(Br)Pip)(Br)] (**4**) could be successfully crystallized (*vide infra*, Figure 1), yielding 58% of the pure product.

From the reaction of *trans*-[$(Cy_3P)_2Pt${B(Br)Mes}(Br)] (**5**) and dcpe in C_6H_6 after 5 h at 45 °C *cis*-[(dcpe)Pt{B(Br)-Mes)(Br)] (**6**) precipitated, which was isolated in 58% yield and is characterized by similar $^{31}P\{^1H\}$ NMR data, that is, a broad singlet at 65.4 ppm ($^1J_{P\text{-}Pt}$ = 1187 Hz) and a doublet at 53.5 ppm ($^1J_{P\text{-}Pt}$ = 4108 Hz, $^2J_{P\text{-}P}$ = 5 Hz). A single crystal, obtained from a CH_2Cl_2/hexane mixture at −35 °C, could be analyzed by X-ray diffraction (*vide infra*, Figure 1). However, if the same reaction is carried out in CH_2Cl_2 rather than C_6H_6, the initially formed *cis*-[(dcpe)Pt{B(Br)Mes)(Br)] (**6**) reacts with the solvent in the presence of PCy_3 within 6 days with halogen exchange at the boron center and formation of [(dcpe)Pt{B(Cl)Mes)(Br)] (**7**). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture features

(8) Charmant, J. P. H.; Fan, C.; Norman, N. C.; Pringle, P. G. *Dalton Trans.* **2007**, 114–123.
(9) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Organometallics* **2004**, *23*, 5545–5549.
(10) Braunschweig, H.; Radacki, K.; Uttinger, K. *Inorg. Chem.* **2007**, *46*, 8796–8800.
(11) Zhu, J.; Lin, Z.; Marder, T. B. *Inorg. Chem.* **2005**, *44*, 9384–9390.
(12) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5651–5654. (b) Braunschweig, H.; Brenner, P.; Mueller, A.; Radacki, K.; Rais, D.; Uttinger, K. *Chem.−Eur. J.* **2007**, *13*, 7171–7176.
(13) (a) Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658–1660. (b) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F.; Uttinger, K. *J. Am. Chem. Soc.* **2005**, *127*, 1386–1387. (c) Braunschweig, H.; Whittell, G. R. *Chem.−Eur. J.* **2005**, *11*, 6128–6133.
(14) Braunschweig, H.; Radacki, K.; Uttinger, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3979–3982.
(15) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 1066–1069. (b) Braunschweig, H.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3763–3766. (c) Braunschweig, H.; Burschka, C.; Burzler, M.; Radacki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4352–4355. (d) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Organometallics* **2006**, *25*, 5159–5164. (e) Braunschweig, H.; Radacki, K.; Uttinger, K. *Eur. J. Inorg. Chem.* **2007**, *27*, 4350–4356.
(16) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1192–1194.
(17) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 162–165. (b) Braunschweig, H.; Radacki, K.; Rais, D.; Schneider, A.; Seeler, F. *J. Am. Chem. Soc.* **2007**, *129*, 10350–10351.
(18) Fischer, R. A.; Weiss, D.; Winter, M.; Mueller, I.; Kaesz, H. D.; Froehlich, N.; Frenking, G. *J. Organomet. Chem.* **2004**, *689*, 4611–4623.
(19) (a) Zanardo, A.; Michelin, R. A.; Pinna, F.; Strukul, G. *Inorg. Chem.* **1989**, *28*, 1648–1653. (b) Crociani, B.; Di Bianca, F.; Giovenco, A.; Berton, A.; Bertani, R. *J. Organomet. Chem.* **1989**, *361*, 255–267.

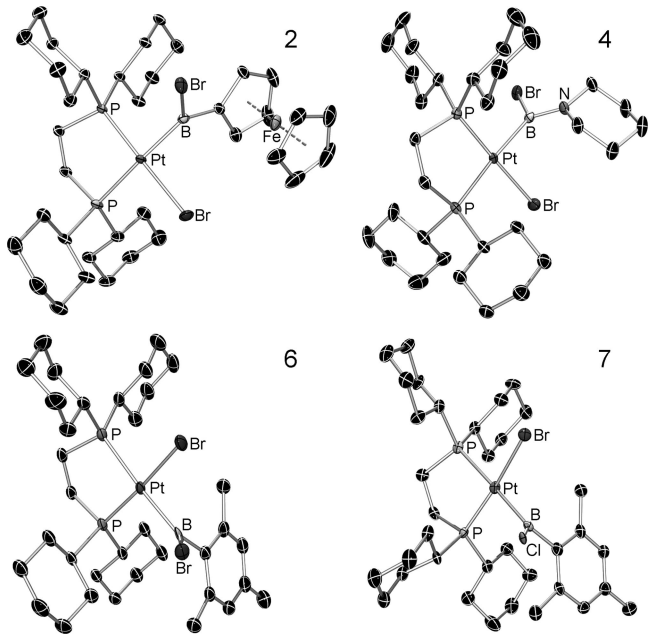


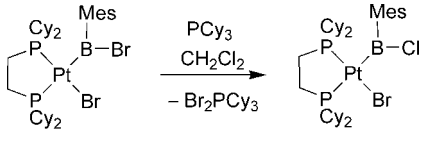
Figure 1. Molecular structures of the *cis*-bromoboryl complexes. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are at the 50% probability level. In **7** the boryl moiety is disordered (i.e., the boryl ligand is twisted by 8° with respect to the position in Figure 1, due to thermal rotation/fluctuation). Important bond lengths are shown in Table 1.

Table 1. Important Bond Lengths (in Å) of the Compounds 2, 4, 6, and 7

	Pt−P (*trans* B)	Pt−P (*cis* B)	Pt−B	Pt−Br	B−Hal
2: B(Fc)Br	2.3716(8)	2.2165(7)	2.004(3)	2.4839(3)	1.988(3)
4: B(Pip)Br	2.3567(8)	2.2148(8)	2.068(3)	2.5044(3)	2.011(3)
6: B(Mes)Br	2.3632(10)	2.2225(10)	2.132(4)	2.495(4)	1.978(4)
7: B(Mes)Cl	2.367(3)	2.223(2)	2.113(10)	2.5002(10)	1.777(10)

a peak at 103 ppm, indicating the formation of Br_2PCy_3,[20] a broad singlet at 65.4 ($^1J_{P\text{-}Pt}$ = 1187 Hz), and a doublet at 53.5 ($^1J_{P\text{-}Pt}$ = 4108 Hz, $^2J_{P\text{-}P}$ = 2 Hz) for **7**. *cis*-[(dcpe)Pt{B(Cl)Mes)(Br)] (**7**) could be isolated in 61% yield, and crystals suitable for X-ray analysis were grown from a CH_2Cl_2/hexane mixture at −35 °C (*vide infra*, Figure 1).

Scheme 2. Conversion of *cis*-[(dcpe)Pt{B(Br)Mes)(Br)] (6) into *cis*-[(dcpe)Pt{B(Cl)Mes)(Br)] (7) in the Presence of PCy_3 in CH_2Cl_2



6 **7**

All of the aforementioned dcpe complexes **2**, **4**, **6**, and **7** possess two chemically nonequivalent phosphorus atoms and, thus, should exhibit two doublets in the $^{31}P\{^1H\}$ NMR spectra. Due to unresolved coupling with the quadrupolar boron nucleus, however, the resonances for the phosphorus atoms in *trans*-position to the boryl ligand are very broad, thus precluding the resolution of the expected doublet. The $^2J_{P\text{-}P}$ coupling for the phosphorus atom *trans* to bromide was found to be very small (≤5 Hz) and was thus only detected in the case of the mesityl species **6** and **7**. All of these spectroscopic characteristics as well as the significant differences of the two $^1J_{P\text{-}Pt}$ couplings observed here for each complex have ample precedence in the literature and were reported, for example, for *cis*-[$(R_3P)_2$Pt-(BPin)($SiMe_2$Ph)],[7] [(dcpe)Pt(Cl)(CH_2CMe_3)],[21] and [(dppe)Pt-(Cl)(Me)],[22] respectively. It should be noted that the $^1J_{P\text{-}Pt}$ coupling constants for the phosphorus atom *trans* to boron are extremely small (**2**: 1098, **4**: 1187, **6**: 1056, **7**: 1047 Hz) compared to other square-planar Pt(II) complexes. Even ligands that exhibit a strong *trans*-influence and, thus, impose relatively small couplings, such as in *cis*-[$(Ph_3P)_2$Pt($BNMe_2$)($GeMe_3$)] (1200 Hz (P *trans* to Ge)),[6] *cis*-[$(Me_3P)_2$Pt(BPin)($SiMe_2$Ph)] (1374 Hz (P *trans* to Si)), and *cis*-[(dcpe)Pt(AlR_2)(R)] (R = CH_2CMe_3) (1222 Hz (P *trans* to Al)),[18] give rise to greater values for $^1J_{P\text{-}Pt}$. All additional multinuclear NMR data, such as the broad $^{11}B\{^1H\}$ NMR reasonances (**2**: 94, **4**: 49, **6**: 100, **7**: 103 ppm), that are significantly deshielded with respect to those of the starting bromoboranes are unobtrusive and meet with the expectations.

Structural Characterization. The compounds **2** and **7** crystallize in the monoclinic $P2_1/c$, **4** in the orthorhombic *Pbca*, and **6** in the triclinic $P\bar{1}$ space group. All boryl ligands (defined by the BR_2 plane) adopt the preferential, almost perpendicular arrangement with respect to the PtP_2 plane (dihedral angles **2**: 76.68°; **4**: 80.20°; **6**: 70.24°; **7**: 78.69°), thus allowing for maximum overlap between the occupied platinum d_{xy} and vacant p-orbital at boron.[3d] To avoid steric repulsion, the bulky mesityl groups in **6** and **7** are twisted with respect to the BR_2 planes, as indicated by the corresponding dihedral angles of 50.20° (**6**) and 46.19° (**7**).

The Pt−B bond distances (**2**: 2.044(3), **4**: 2.068(3), **6**: 2.132(4), **7**: 2.113(10) Å) are somewhat greater than in the corresponding starting materials *trans*-[$(Cy_3P)_2$Pt{B(Br)R}(Br)] (**1**: 1.944(3), **3**: 2.021(5), **5**: 2.009(3) Å)[12b] and, thus, comparable to other Pt complexes bearing phosphines in *trans*-position to a boryl moiety, e.g., *cis*-[$(Ph_3P)_2$Pt($BCat)_2$] and *cis*-[$(Ph_3P)_2$Pt-($BNMe_2$)($SnMe_3$)].[5c,6] As expected, the Pt−Br distances in the products are in the range of about 2.50 Å (Table 1), thus being significantly smaller than in the corresponding *trans* boryl complexes (2.6141(3)−2.6313(5) Å),[12b] reflecting the much smaller *trans*-influence of phosphine ligands in comparison to boryls (*vide supra*).

The most notable structural feature of the complexes **2**, **4**, **6**, and **7** is the pronounced difference between both Pt−P separations in each molecule. The Pt−P distances *trans* to the boron centers (Table 1) are approximately 15 pm greater than those *trans* to bromide, as an effect of the strong *trans*-influence of the boryl group. The theoretically predicted[11] and in the case of the *trans*-complexes **1**, **3**, and **5** experimentally proven trend[12b] that B(aryl) ligands impose a stronger *trans*-influence than $B(NR_2)$-based groups becomes apparent here as well, however, to a much lesser extent, as the observed differences in Pt−B bond lengths for **2**, **4**, **6**, and **7** are very small and lie almost in the range of the respective standard deviations.

In conclusion, the conversion of several *trans*-haloboryl complexes to their *cis*-analogues was accomplished by the reaction with an appropriate chelating phosphine, thus giving rise to a set of unprecedented, fully characterized *cis*-(bromo)boryl complexes, *cis*-[(dcpe)Pt{B(X)R)(Br)] (R = Fc, Pip,

(20) Godfrey, S. M.; McAuliffe, C. A.; Mushtaq, I.; Pritchard, R. G.; Sheffield, J. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3815–3818.

(21) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448.

(22) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439–446.

Mes, X = Br; R = Mes, X = Cl). The distinct differences in the Pt−P bond lengths observed in the solid state structures can be ascribed to the strong *trans*-influence of the boryl groups. Studies directed toward the utilization of such compounds and derivatives thereof in catalytic processes are underway in our laboratories.

Experimental Section

All manipulations were performed either under dry argon or *in vacuo* using standard Schlenk line and glovebox techniques. Solvents (toluene, benzene, and hexane) were purified by distillation under dry argon from appropriate drying agents (Na and Na/K alloy, respectively) and stored under the same inert gas over molecular sieves. Deuterated solvents were degassed by three freeze–pump–thaw cycles and stored over molecular sieves. NMR spectra were recorded on a Bruker Avance 500 (^{1}H: 500.13; ^{31}P: 202.46; ^{11}B: 160.47; ^{13}C: 125.77 MHz) NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and ^{31}P{^{1}H} NMR spectra to 85% H_3PO_4. Microanalyses for C, H, and N were performed on a Elementar Vario MICRO cube instrument.

[(dcpe)Pt{B(Br)Fc}(Br)] (2). Solid [Pt(PCy$_3$)$_2$] (0.100 g, 0.132 mmol) and FcBBr$_2$ (0.053 g, 0.149 mmol) were put in a J-Young NMR tube and dissolved in toluene (0.6 mL); the reaction was judged to be complete by ^{31}P{^{1}H} NMR spectroscopy showing a corresponding signal for *trans*-[(Cy$_3$P)$_2$Pt{B(Br)Fc}(Br)] (**1**). Then dcpe (0.060 g, 0.142 mmol) was added to the deep red reaction mixture. Overnight orange crystals formed, which were separated and washed with benzene (2 × 0.3 mL), yielding 90 mg of *cis*-[(dcpe)Pt{B(Br)Fc}(Br)] (**3**) (71%).

^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): δ 4.60 (m, 1H, C_5H_4B), 4.55 (m, 1H, C_5H_4B), 4.51 (m, 1H, C_5H_4B), 4.43 (m, 1H, C_5H_4B), 4.29 (s, 5H, C_5H_5), 2.50−0.60 (m, 48H, dcpe). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 24 °C): δ 87.2 (br s, C_{ipso}, C_5H_4B, from 2D-HMBC), 77.3 (s, C_5H_4B), 76.6 (s, C_5H_4B), 73.2 (s, C_5H_4B), 72.1 (s, C_5H_4B), 70.3 (s, C_5H_5), 35.8–34.2 (complex superpositions, C1, dcpe), 30.1−25.5 (complex superpositions, dcpe), 26.1 (dd, $^1J_{C\text{-}P}$ = 33 Hz, $^3J_{C\text{-}P}$ = 23 Hz, P-CH$_2$, dcpe), 19.3 (dd, $^1J_{C\text{-}P}$ = 19 Hz, $^3J_{C\text{-}P}$ = 6 Hz, P-CH$_2$, dcpe). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 24 °C): δ 94 (br s, ω½ ≈ 1560 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 24 °C): δ 65.0 (br s, $^1J_{P\text{-}Pt}$ = 1098 Hz), 52.0 (s, $^1J_{P\text{-}Pt}$ = 4140 Hz). Anal. Calcd for $C_{36}H_{57}BBr_2FeP_2Pt$: C, 44.42; H, 5.90. Found: C, 44.96; H, 5.60.

[(dcpe)Pt{B(Br)Pip}(Br)] (4). Solid [Pt(PCy$_3$)$_2$] (0.109 g, 0.144 mmol) was dissolved in toluene (0.6 mL) in a J-Young NMR tube, and PipBBr$_2$ (0.038 g, 0.149 mmol) was added; the reaction was judged to be complete by ^{31}P{^{1}H} NMR spectroscopy showing a signal for *trans*-[(Cy$_3$P)$_2$Pt{B(Br)Pip}(Br)] (**3**). Then dcpe (0.070 g, 0.166 mmol) was added to the yellow reaction mixture and heated at 80 °C for 1 week. The white solid was removed and the solution was allowed to evaporate slowly. After 2 weeks benzene (1 mL) was added to the oily residue and the solvent was allowed to evaporate slowly. Colorless solid formed after 3 days, which was washed with hexane (3 × 1 mL), yielding 75 mg (58%) of *cis*-[(dcpe)Pt{B(Br)Pip}(Br)] (**4**).

^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 4.59(m, 2H, NCH$_2$, C-1 and C-2 Pip), 3.29 (m, 1H, NCH$_2$, C-1 Pip), 2.97 (m, 1H, NCH$_2$, C-2 Pip), 2.81 (m, 1H, Pip), 2.65 (m, 1H, dcpe), 2.40−1.00 (m, 52H, Pip and dcpe). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 23 °C): δ 56.1 (s, NCH$_2$, C-1), 51.6 (s, NCH$_2$, C-2), 36.2−34.2 (complex superpositions, C1, dcpe), 30.8−26.0 (complex superpositions, Pip and dcpe), 19.7 (dd, $^1J_{C\text{-}P}$ = 20 Hz, $^3J_{C\text{-}P}$ = 7 Hz, P-CH$_2$, dcpe). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 23 °C): δ 49 (br s). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 23 °C): δ 65.3 (br s, $^1J_{P\text{-}Pt}$ = 1187 Hz), 53.5 (s, $^1J_{P\text{-}Pt}$ = 4108 Hz). Anal. Calcd for $C_{33}H_{58}BBr_2NP_2Pt$: C, 44.21; H,6.52; N 1.56. Found: C, 44.70; H, 6.89; N 1.56.

[(dcpe)Pt{B(Mes)Br}(Br)] (6). Solid *trans*-[(Cy$_3$P)$_2$Pt{B(Br)-Mes}(Br)] (**5**) (0.050 g, 0.048 mmol) was suspended in benzene (0.6 mL) in a J-Young NMR tube, and dcpe (0.020 g, 0.048 mmol) was added. After warming at 45 °C for 3 h the reaction was judged to be complete by ^{31}P{^{1}H} NMR. After 2 days pale yellow crystalline material precipitated, which was recrystallized from a CH_2Cl_2/hexane mixture at −35 °C. Colorless crystals could be obtained after 2 days, yielding 25 mg (58%) of *cis*-[(dcpe)Pt{B(Br)Mes}(Br)] (**6**).

^{1}H NMR (500 MHz, CD_2Cl_2, 24 °C): δ 6.75 (2 overlapping s, 2H, C_{meta}H, Mes), 2.56 (s, 6H, C_{ortho}-CH$_3$, Mes), 2.31 (m, 2H, dcpe), 2.23 (s, 3H, C_{para}-CH$_3$, Mes), 2.15 (m, 2H, dcpe), 2.04 (m, 2H, dcpe), 1.88−0.75 (m, 42H, dcpe). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 24 °C,): δ 150.0 (br s, C_{ipso}, Mes, from 2D-HMBC), 138.6 (s, C_{ortho}, Mes), 136.8 (s, C_{para}, Mes), 128.8 (s, C_{meta}, Mes), 37.5 (dd, $^1J_{C\text{-}P}$ = 35 Hz, $^3J_{C\text{-}P}$ = 2 Hz, C1, dcpe), 34.5 (d, $^1J_{C\text{-}P}$ = 18 Hz, C1, dcpe), 30.4 (s, C3–5, dcpe), 29.6 (d, $^3J_{C\text{-}P}$ = 4 Hz, C3–5, dcpe), 29.4 (d, $^3J_{C\text{-}P}$ = 3 Hz, C3–5, dcpe), 29.0 (d, $^3J_{C\text{-}P}$ = 2 Hz, C3–5, dcpe), 27.5 (d, $^2J_{C\text{-}P}$ = 13 Hz, C2–6, dcpe), 27.4 (d, $^2J_{C\text{-}P}$ = 9 Hz, C2–6, dcpe), 27.3 (d, $^2J_{C\text{-}P}$ = 10 Hz, C2–6, dcpe), 26.8 (d, $^2J_{C\text{-}P}$ = 14 Hz, C2–6, dcpe), 26.5 (d, $^4J_{C\text{-}P}$ = 1 Hz, C4, dcpe), 26.3 (d, $^4J_{C\text{-}P}$ = 1 Hz, C4, dcpe), 25.8 (s, C_{ortho}-*C*H$_3$, Mes), 24.6 (dd, $^1J_{C\text{-}P}$ = 34 Hz, $^3J_{C\text{-}P}$ = 23 Hz, P-CH$_2$, dcpe), 21.0 (s, C_{para}-*C*H$_3$, Mes), 18.8 (dd, $^1J_{C\text{-}P}$ = 20 Hz, $^3J_{C\text{-}P}$ = 5 Hz, P-CH$_2$, dcpe). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 24 °C): δ 103 (br s, ω½ ≈ 1470 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 24 °C): δ 65.4 (br s, $^1J_{P\text{-}Pt}$ = 1056 Hz), 53.6 (d, $^1J_{P\text{-}Pt}$ = 4025 Hz, $^3J_{P\text{-}P}$ = 5 Hz). Anal. Calcd for $C_{35}H_{59}BBr_2P_2Pt$: C, 46.32; H, 6.55. Found: C, 46.20; H, 6.32.

[(dcpe)Pt{B(Cl)Mes}(Br)] (7). Solid *trans*-[(Cy$_3$P)$_2$Pt{B(Br)-Mes}(Br)] (**5**) (0.100 g, 0.096 mmol) was dissolved in CH_2Cl_2 (0.6 mL) in a J-Young NMR tube, and dcpe (0.040 g, 0.096 mmol) was added. After 3 h the reaction was judged to be complete, showing the corresponding signals for *cis*-[(dcpe)Pt{B(Br)Mes}-(Br)] (**6**) in the ^{31}P{^{1}H} NMR spectrum. After 3 days the new compound *cis*-[(dcpe)Pt{B(Cl)Mes}(Br)] (**7**) can be detected by ^{31}P{^{1}H} NMR spectroscopy. After another 3 days the conversion was complete. The solvent was allowed to evaporate slowly, and after 4 days the solid was washed with C_6H_6 (3 × 0.3 mL), yielding 50 mg (61%) of *cis*-[(dcpe)Pt{B(Cl)Mes}(Br)] (**7**). Crystals suitable for an X-ray diffraction analysis could be prepared by recrystallization from a CH_2Cl_2/hexane mixture at −35 °C.

^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ 6.75 (2 overlapping s, 2H, C_{meta}H, Mes), 2.59 (s, 6H, C_{ortho}-CH$_3$, Mes), 2.29 (m, 2H, dcpe), 2.22 (s, 3H, C_{para}-CH$_3$, Mes), 2.12 (m, 2H, dcpe), 1.96 (m, 2H, dcpe), 1.88−0.75 (m, 42H, dcpe). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 23 °C): δ 148.2 (br s, C_{ipso}, Mes), 138.6 (s,C_{ortho}, Mes), 138.1 (s, C_{para}, Mes), 128.8 (s,C_{meta}, Mes), 37.3 (dd, $^1J_{C\text{-}P}$ = 35 Hz, $^3J_{C\text{-}P}$ = 2 Hz, C1, dcpe), 34.3 (d, $^1J_{C\text{-}P}$ = 17 Hz, C1, dcpe), 30.1 (s, C3–5, dcpe), 29.5 (d, $^3J_{C\text{-}P}$ = 4 Hz, C3–5, dcpe), 29.2 (d, $^3J_{C\text{-}P}$ = 4 Hz, C3–5, dcpe), 28.9 (d, $^3J_{C\text{-}P}$ = 1 Hz, C3–5, dcpe), 27.5 (d, $^2J_{C\text{-}P}$ = 10 Hz, C2–6, dcpe), 27.4 (d, $^2J_{C\text{-}P}$ = 6 Hz, C2–6, dcpe), 27.3 (d, $^2J_{C\text{-}P}$ = 10 Hz, C2–6, dcpe), 26.8 (d, $^2J_{C\text{-}P}$ = 14 Hz, C2–6, dcpe), 26.5 (d, $^4J_{C\text{-}P}$ = 1 Hz, C4, dcpe), 26.3 (d, $^4J_{C\text{-}P}$ = 1 Hz, C4, dcpe), 25.8 (s, C_{ortho}-*C*H$_3$, Mes), 25.1 (dd, $^1J_{C\text{-}P}$ = 33 Hz, $^3J_{C\text{-}P}$ = 23 Hz, P-CH$_2$, dcpe), 21.1 (s, C_{para}-*C*H$_3$, Mes), 18.9 (dd, $^1J_{C\text{-}P}$ = 20 Hz, $^3J_{C\text{-}P}$ = 5 Hz, P-CH$_2$, dcpe). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 23 °C): δ 100 (br s, ω½ ≈ 1330 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, 23 °C): δ 65.7 (br s, $^1J_{P\text{-}Pt}$ = 1047 Hz), 53.5 (d, $^1J_{P\text{-}Pt}$ = 4094 Hz, $^3J_{P\text{-}P}$ = 2 Hz). Anal. Calcd for $C_{35}H_{59}BBrClP_2Pt$: C, 48.71; H, 6.89. Found: C, 49.01; H, 6.96.

Crystal Structure Determination. The crystal data of **2**, **4**, **6**, and **7** were collected on a Bruker X8Apex diffractometer with CCD area detector and multilayer mirror monochromated Mo Kα radiation. 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.

Crystal data for **2**: $C_{36}H_{57}BBr_2FeP_2Pt$, $M_r = 973.33$, orange blocks, 0.29 × 0.28 × 0.17, monoclinic space group $P2_1/c$, $a = 12.1129(8)$ Å, $b = 14.2546(9)$ Å, $c = 21.6898(15)$ Å, $\beta = 92.097(3)°$, $V = 3742.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.727$ g·cm^{-3}, $\mu = 6.366$ mm^{-1}, $F(000) = 1928$, $T = 98(2)$ K, $R_1 = 0.0422$, $wR_2 = 0.0772$, 11 695 independent reflections [$2\theta \leq 63.88°$] and 388 parameters.

Crystal data for **4**: $C_{31}H_{58}BBr_2NP_2Pt \cdot (C_7H_8)$, $M_r = 964.58$, colorless plates, 0.220 × 0.210 × 0.120, orthorhombic space group *Pbca*, $a = 17.1174(4)$ Å, $b = 19.8926(4)$ Å, $c = 23.6733(6)$ Å, $V = 8061.0(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.590$ g·cm^{-3}, $\mu = 5.570$ mm^{-1}, $F(000) = 3872$, $T = 100(2)$ K, $R_1 = 0.0389$, $wR_2 = 0.0659$, 11 403 independent reflections [$2\theta \leq 59.38°$] and 418 parameters.

Crystal data for **6**: $C_{35}H_{59}BBr_2P_2Pt \cdot 2.5(C_6H_6)$, $M_r = 1102.75$, colorless needles, 0.18 × 0.065 × 0.065, triclinic space group $P\bar{1}$, $a = 8.6839(3)$ Å, $b = 16.0549(5)$ Å, $c = 17.7870(6)$ Å, $\alpha = 78.295(2)°$, $\beta = 81.914(2)°$, $\gamma = 76.596(2)°$, $V = 2350.69(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.558$ g·cm^{-3}, $\mu = 4.786$ mm^{-1}, $F(000) = 1114$, $T = 100(2)$ K, $R_1 = 0.0442$, $wR_2 = 0.1021$, 13 550 independent reflections [$2\theta \leq 65.88°$] and 508 parameters.

Crystal data for **7**: $C_{35}H_{59}BBrClP_2Pt \cdot 2(CH_2Cl_2)$, $M_r = 1032.87$, colorless needles, 0.18 × 0.08 × 0.06, monoclinic space group $P2_1/c$, $a = 8.6923(13)$ Å, $b = 17.456(2)$ Å, $c = 27.895(4)$ Å, $\beta = 92.335(7)°$, $V = 4229.0(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.622$ g·cm^{-3}, $\mu = 4.680$ mm^{-1}, $F(000) = 2072$, $T = 99(2)$ K, $R_1 = 0.0946$, $wR_2 = 0.1646$, 8244 independent reflections [$2\theta \leq 52.22°$] and 464 parameters.

Acknowledgment. This work was supported by the DFG and the Fonds der Chemischen Industrie.

Supporting Information Available: Crystallographic data (CIF files) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 662542−5. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or at http://pubs.acs.org.

OM700976T