Inorg. Chem. **2007**, *46*, 8796–8800

Inorganic Chemistry Article

Syntheses of Mono- and Dinuclear Diiodoboryl Complexes of Platinum

Holger Braunschweig,* Krzysztof Radacki, and Katharina Uttinger

Julius-Maximilians Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Received June 5, 2007

Treatment of [Pt(PCy_3)$_2$] (Cy = cyclohexyl) with BI_3 afforded *trans*-[(Cy_3P)$_2$Pt(I)(BI_2)] by the oxidative addition of a B–I bond. The title compound represents the first diiodoboryl complex and was fully characterized by NMR spectroscopy and X-ray diffraction analysis. The latter revealed a very short Pt–B distance, thus indicating a pronounced π contribution to this bond. By the addition of another 1 equiv of BI_3 to *trans*-[(Cy_3P)$_2$Pt(I)(BI_2)], a new Pt species [(Cy_3P)(I_2B)Pt(μ-I)]$_2$ was formed with concomitant buildup of the phosphine borane adduct [Cy_3P–BI_3]. The former is obviously obtained by abstraction of PCy_3 from *trans*-[(Cy_3P)$_2$Pt(I)(BI_2)] and the subsequent dimerization of two remaining fragments. Interestingly, the dimerization is reversible, and the dinuclear compound can be converted to *trans*-[(Cy_3P)$_2$Pt(I)(BI_2)] upon the addition of PCy_3.

Introduction

Among the wide variety of boryl complexes, corresponding dihaloboryl species [L_nM-BX_2] represent synthetically rather challenging targets, most of which were only recently achieved.[1] Spectroscopically fully characterized difluoroboryl complexes such as [(η^5-C_5Me_5)IrH(BF_2)(PMe_3)] were first reported by Bergman et al.,[2] while Norman and co-workers recently described *cis*-[(Ph_3P)$_2$Pt(BF_2)$_2$] and *fac*-[(Ph_3P)$_2$(OC)Ir(BF_2)$_3$], which were prepared by the oxidative addition of B_2F_4 to Pt(0) or Ir(I) precursors.[3] In the case of these difluoro derivatives, no further functionalization is reported so far, presumably due to the high thermodynamic stability of the B−F bond and the decreased Lewis acidity of the boron center.

However, dichloro- and dibromoboryl complexes provide an interesting chemistry and were already utilized as precursors for a variety of substitution and addition reactions at the metal-coordinated Hal_2B group (Hal = halogen), thus leading to highly unusual coordination modes of boron-centered ligands. For example, the addition of 8-aminoquinoline to the dichloroboryl complex [(Ph_3P)$_2$(OC)Os(BCl_2)Cl] afforded a base-stabilized borylene complex, which was reported by Roper et al. Further substitution chemistry resulted in a range of tethered boryl- and base-stabilized borylene compounds.[4] Recently, a series of dichloroboryl complexes *trans*-[(R_3P)$_2$Pt(Cl)(BCl_2)] (R_3 = Ph_3, Ph_2Me, $PhMe_2$, Me_3) were obtained by reacting the corresponding Pt(0) species with BCl_3. The latter shows reactivity toward Lewis bases, forming *trans*-[(Me_3P)$_2$Pt(Cl){BCl_2(L)}] (L = NEt_3, NC_5H_5), and the substitution of one or two boron-bound chlorides by $HNEt_2$, piperidine, or catechol is also possible.[5]

Our group succeeded in preparing iron and manganese complexes via the salt elimination of corresponding carbonylates and BX_3 (X = Br, Cl) or $BF_3\cdot OEt_2$, resulting in the formation of [(η^5-C_5R_5)(OC)$_2$Fe(BX_2)] (R = H, Me; X = F, Cl, Br) and [(OC)$_5$Mn(BX_2)] (X = Cl, Br).[6] Of these, [(η^5-C_5H_5)(OC)$_2$Fe(BCl_2)] was the first dichloroboryl complex

---

* To whom correspondence should be addressed. E-mail: h.braunschweig@mail.uni-wuerzburg.de. Tel: +49 931 888 5260. Fax: +49 931 888 4623.

(1) (a) Irvine, G. I.; 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. (b) Braunschweig, H.; Colling, M. *Coord. Chem. Rev.* **2001**, *223*, 1−51. (c) Braunschweig, H. *Angew. Chem.* **1998**, *110*, 1882−1898. Braunschweig, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1786−1801. (d) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535−559. (e) Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem.* **2006**, *118*, 5380−5400. Braunschweig, H.; Kollann, C.; Rais, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 5254−5274.

(2) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005−2020.

(3) (a) 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. (b) 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.

(4) (a) Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem.* **2000**, *112*, 978−980. Irvine, G. J.; Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 948−950. (b) Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2002**, *21*, 4862−4872. (c) Clark, G. R.; Irvine, G. J.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2003**, *680*, 81−88.

(5) Charmant, J. P. H.; Fan, C.; Norman, N. C.; Pringle, P. G. *Dalton Trans.* **2007**, 114−123.

(6) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2006**, *25*, 4605−4610.

10.1021/ic7011028 CCC: $37.00

to be structurally characterized by X-ray diffraction,[7] while spectroscopic evidence was initially reported by Aldridge et al.[8] Despite its coordination to the potentially π-donating metal fragment, Lewis bases can be added to the boron atom, and compounds such as $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{BX_2(NC_5H_4\text{-}4\text{-}Me)\}]$ (X = Cl, Br) were isolated.[6,7] In addition, dichloro- and dibromoboryl complexes served as precursors for metalloborylenes $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe(\mu^2\text{-}B)M(CO)_n]$ (M = Cr, n = 5; M = Fe, n = 4)[9] and metal-base-stabilized metalloborylenes $[(\eta^5\text{-}C_5Me_5)(OC)Fe(\mu\text{-}CO)M(PCy_3)(\mu\text{-}Br)\text{-}Pt(PCy_3)Br(\mu^3\text{-}B)]$ (M = Pd, Pt; Cy = cyclohexyl),[10] where the boron atom is exclusively coordinated to two or three transition metals. Aside from those, bridging boryl $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)_2(\mu\text{-}BCl_2)Pd(PCy_3)]$[11] and heterodinuclear borylene complexes $[(\eta^5\text{-}C_5Me_5)Fe(CO)(\mu\text{-}CO)(\mu\text{-}BBr)PdBr\text{-}(PCy_3)]$[12] were obtained.

Despite recent advances in the preparation of dihaloboryl complexes, fully characterized transition-metal compounds displaying B−I bonds are still absent. Herein, we report on the synthesis and full characterization of two diiodoboryl complexes, obtained by the oxidative addition of BI_3 to $[Pt(PCy_3)_2]$.

Discussion

In an extension of our recent work on boryl complexes being obtained by the oxidative addition of B−Br bonds to late transition metals,[12,13] $[Pt(PCy_3)_2]$ was reacted with equimolar amounts of BI_3, and multinuclear NMR spectroscopy of the benzene reaction mixture revealed the complete consumption of the starting materials and the predominant formation of one new species. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at 10.3 ppm flanked by Pt satellites (J = 2737 Hz), with the coupling constant possessing a typical magnitude for boryl complexes with phosphine ligands in mutual trans disposition.[5,13,14] In addition, a broad resonance at −26.6 ppm could be observed, indicating the presence of the phosphine borane adduct $[Cy_3P{-}BI_3]$ (**1**) (vide infra). After 15 min, some fine white powder precipitated from the red-brown solution, which was separated and washed with hexane and turned out to be the desired product *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$ (**2**) (41% yield) (Scheme 1). The $^{11}B\{^1H\}$ NMR spectrum of the isolated material featured a broad signal at 31.0 ppm, and the $^{13}C\{^1H\}$ and ^1H NMR data showed appropriate resonances for the cyclohexyl groups.

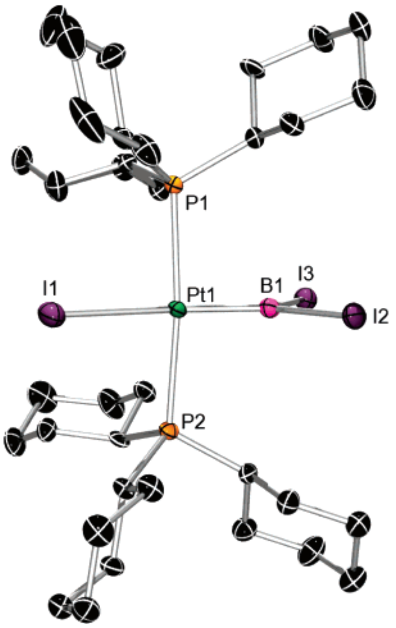
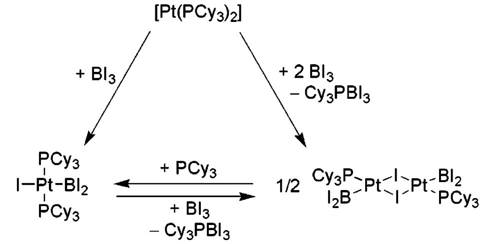


Figure 1. Molecular structure of **2**. Thermal ellipsoids at 50% probability level. The unit cell contains two independent molecules and one molecule of C_6H_6. Only one molecule is represented, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−B1 1.947(8), Pt1−P1 2.3524(15), Pt1−P2 2.3579(15), Pt1−I1 2.7813(7), B1−I2 2.189(7), B1−I3 2.185(8), B1−Pt1−P1 90.3(2), P1−Pt1−I1 91.63(4), P1−Pt1−P2 165.31(6), B1−Pt1−I1 168.2(2), I3−B1−I2 110.4(3), Pt1−B1−I2 129.1(4), Pt1−B1−I3 120.5(4), P1−Pt1−B1−I2 97.8(3); Pt1′−B1′ 1.952(7), Pt1′−P1′ 2.3561(17), Pt1′−P2′ 2.3627(17), Pt1′−I1′ 2.7495(6), B1′−I2′ 2.196(7), B1′−I3′ 2.183(7), B1′−Pt1′−P1′ 90.7(2), P1′−Pt1′−I1′ 90.23(4), P1′−Pt1′−P2′ 167.22(6), B1′−Pt1′−I1′ 169.6(2), I3′−B1′−I2′ 110.1(3), Pt1′−B1′−I2′ 129.5(4), Pt1′−B1′−I3′ 120.4(4), P1′−Pt1′−B1′−I2′ 97.5(4).

Scheme 1. Formation of **2** and **3**.



Single crystals suitable for X-ray diffraction analysis were obtained from a benzene solution by slow evaporation, and the molecular structure is shown in Figure 1. The molecule crystallizes in the space group C_2/c and adopts a slightly distorted square-planar geometry around platinum and a mutual trans arrangement of the phosphine ligands. (The parameters of only one of two independent molecules found in the unit cell will be considered in this discussion, whereas

---

(7) Braunschweig, H.; Radacki, K.; Seeler, F.; Whittell, G. R. *Organometallics* **2004**, *23*, 4178−4180.

(8) (a) Aldridge, S.; Calder, R. J.; Baghurst, R. E.; Light, M. E.; Hursthouse, M. B. *J. Organomet. Chem.* **2002**, *649*, 9−14. (b) Aldridge, S.; Calder, R. J.; Coles, S. J.; Hursthouse, M. B. *J. Chem. Crystallogr.* **2003**, *33*, 805−810.

(9) (a) Braunschweig, H.; Radacki, K.; Scheschkewitz, D.; Whittell, G. R. *Angew. Chem.* **2005**, *117*, 1685−1688. *Angew. Chem., Int. Ed.* **2005**, *44*, 1658−1660. (b) Braunschweig, H.; Whittell, G. R. *Chem.—Eur. J.* **2005**, *11*, 6128−6133.

(10) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem.* **2006**, *118*, 1087−1090. Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 1066−1069.

(11) Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem.* **2005**, *117*, 1217−1219. Braunschweig, H.; Radacki, K.; Rais, D.; Whittell, G. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1192−1194.

(12) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F.; Uttinger, K. *J. Am. Chem. Soc.* **2005**, *127*, 1386−1387.

(13) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Seeler, F., *Organometallics* **2004**, *23*, 5545−5549. (b) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem.* **2006**, *118*, 169−172. Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 162−165. (c) Braunschweig, H.; Radacki, K.; Uttinger, K. *Angew. Chem.* **2007**, *119*, 4054−4057. Braunschweig, H.; Radacki, K.; Uttinger, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3979−3982. (d) Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. *Angew. Chem.* **2005**, *117*, 5796−5799. Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5651−5654.

(14) 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.

the important data from the second molecule can be found in the figure caption.)

The diiodoboryl group is oriented almost perpendicular to the PtP_2I fragment, as indicated by the torsion angle P1−Pt1−B1−I2 of 97.8(3)°. The most noticeable structural feature is the Pt1−B1 distance of 1.947(8) Å, which is very small compared with that of the other complexes of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Br)R\}]$ (R = Fc = ferrocenyl, distance = 1.9963(34) Å;[13a] R = Mes = mesityl, distance = 2.009(4) Å),[13c] *trans*-$[(Cy_3P)_2Pt\{B(Br)Fc\}][BAr^f_4]$ (Ar^f = 3,5-C_6H_3-$(CF_3)_2$; distance = 1.966(4) Å),[13d] or *trans*-$[(Ph_3P)_2Pt(Cl)(BCat)]$ (Cat = catecholato; distance = 2.008(8) Å).[14] Likewise, even dichloroboryl complexes of the type *trans*-$[(R_3P)_2Pt(Cl)(BCl_2)]$ display a longer Pt−B bond (1.963(6)−1.988(3) Å).[5] The significantly reduced Pt−B separation observed here reflects the less-effective B−Hal π overlapping in the case of iodine in comparison with the smaller halogens and oxygen, thus imposing an increased Pt−B π back-donation. The B−I bonds (B1−I2 = 2.189(7) Å, B1−I3 = 2.185(8) Å) are slightly elongated with comparison to those in the only structurally characterized compound possessing a BI_2 moiety, i.e., $[(I_2B)(Me)(H)C)]_2BI$ (BI_2, B3−I2 = 2.13(1) Å, B3−I3 = 2.12(1) Å; BI, B1−I1 = 2.15(1) Å).[15] The Pt−I bond length of 2.7813(7) Å is remarkably longer (>7 pm) than that in *trans*-$[(Cy_3P)_2PtI_2]$[16] or *trans*-$[(Ph_3P)_2Pt\{CH{=}C(CH_3)_2\}I]$[17] with Pt−I separations of 2.612(1) and 2.709(4) Å, respectively, which is in line with the strong trans influence of the boryl group,[18] whereas the Pt−P distances for *trans*-$[(Cy_3P)_2PtI_2]$[16] and **2** are similar (2.371(2) Å versus 2.3524(15)/2.3579(15) Å).

Interestingly, the formation of the mononuclear complex **2** strongly depends on the stoichiometry of the reaction, as an excess of BI_3 leads to a different product. Initially, after mixing $[Pt(PCy_3)_2]$ and BI_3 in a 1:2 ratio, multinuclear NMR spectroscopy revealed, in addition to the presence of **2** and some unreacted BI_3, the formation of the phosphine borane adduct **1** as indicated by a broad quartet at −26.6 ppm (J = 117 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and a significantly shielded doublet at −74.1 ppm (J = 117 Hz) in the $^{11}B\{^1H\}$ NMR spectrum, as well as a new compound with a $^{31}P\{^1H\}$ NMR resonance at 15.8 ppm indicative of a Pt-bound phosphine (J = 4460 Hz). Heating for 2−3 h at 55 °C led to completion of the reaction as indicated by the gradual decrease of the signal associated with **2** and the concomitant increase of the other two resonances. The spectroscopic data of the new compound are in agreement with its formulation as a dinuclear complex $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ (**3**), which was apparently formed upon the abstraction of PCy_3 from **2** by the Lewis-acidic BI_3 with the subsequent dimerization of two $[(Cy_3P)(I_2B)Pt(I)]$ fragments. Compound **3** was separated from the accompanying adduct **1** by crystallization and repeated rinsing with benzene and was isolated in 43% yield as an analytically pure beige solid. The new dinuclear species **3** proved to be extremely sensitive toward air and moisture and to slowly decompose in solution with formation of red $[Pt_2(\mu\text{-}I)_2I_2(PCy_3)_2]$,[19] as indicated by $^{31}P\{^1H\}$ NMR data. Interestingly, the formation of **3** is reversible: the addition of PCy_3 to a solution of **3** in benzene instantaneously afforded the mononuclear complex **2**, which in return could be converted to the dimer **3** and the adduct **1** by the addition of BI_3 to a benzene solution of **2** and the subsequent heating of the resulting mixture (Scheme 1).

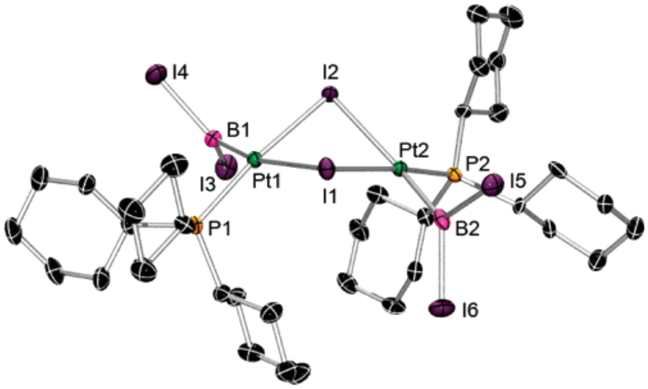


Figure 2. Molecular structure of **3**. Thermal ellipsoids at 50% probability level. Hydrogen atoms and one molecule of C_6H_6 are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−B1 2.002(11), Pt1−P1 2.267(2), Pt1−I1 2.8024(7), Pt1−I2 2.6689(7), B1−I3 2.108(12), B1−I4 2.167(11), Pt2−B2 1.971(12), Pt2−P2 2.268(2), Pt2−I1 2.6646(7), Pt2−I2 2.7962(7), B2−I5 2.182(19), B2−I6 2.151(11), Pt1−I1−Pt2 81.81(2), I1−Pt1−I2 83.74(2), B1−Pt1−I1 168.1(3), P1−Pt1−I2 172.90(6), B1−Pt1−P1 95.2(3), I3−B1−I4 115.3(5), P1−Pt1−B1−I4 92.7(5).

Single crystals of **3** suitable for X-ray diffraction were obtained from a concentrated benzene solution (Figure 2).

In the solid state, both Pt atoms display a slightly distorted square-planar arrangement and the boryl groups are oriented almost orthogonally toward the corresponding PtPI fragment as indicated by the torsion angle from P1−Pt1−B1−I4 of 92.7(5)°. The Pt_2I_2 fragment adopts the geometry of a folded rhombus (123.3° between the two planes of I1−Pt1−I2 and I1−Pt2−I2), a geometry which was observed earlier for $[Rh_2Cl_2(CO)_4]$ or $[\{(F_5C_6)(Ph_3P)Pt(\mu\text{-}PPh_2)(\mu\text{-}I)\}_2Pt]$.[20] The large Pt1−Pt2 distance of 3.582 Å appears to exclude the possibility of any metal−metal interaction.[20b] The Pt−I separations in trans position to the boryl moieties are longer (Pt1−I1 = 2.8024(7) Å, Pt2−I2 = 2.7962(7) Å) than those in trans position to the phosphine ligands (Pt1−I2 = 2.6689(7) Å, Pt2−I1 = 2.6646(7) Å), corroborating the high trans influence of a boryl residue.[18] The longer Pt−I distances are comparable to those in **2**, and the smaller ones are comparable to those in other complexes bearing iodine in trans position to a phosphine group, e.g., $[Pt_2(\mu\text{-}I)_2dppm][BF_4]_2$ with 2.669(1) and 2.662(1) Å[21] or $[Pt_2(\mu\text{-}I)_2I_2(PCy_3)_2]$ with

---

(15) Derforth, T.; Kaschke, M.; Stock, H.; Pritzkow, H.; Siebert, W. *Z. Naturforsch., B: Chem. Sci.* **1997**, *52b*, 823−830.

(16) (a) Alcock, N. W.; Levingston, P. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1834−1836. (b) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2038−2042.

(17) Stang, P. J.; Zhong, Z.; Kowalski, M. H. *Organometallics* **1990**, *9*, 833−838.

(18) Zhu, J.; Lin, Z.; Marder, T. B. *Inorg. Chem.* **2005**, *44*, 9384−9390.

(19) Al−Najjar, I. M. *Inorg. Chim. Acta* **1987**, *128*, 93−104.

(20) (a) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761−1762. (b) Ara, I. Chaouche, N.; Forniés, J.; Consuelo Fortuño, C.; Kribii, A.; Tsipis, A. C.; Tsipis, C. A. *Inorg. Chim. Acta* **2005**, *358*, 1377−1385.

(21) Neve, F.; Crispini, A.; Ghedini, M.; De Munno, G. *Inorg. Chim. Acta* **1990**, *176*, 23−25.

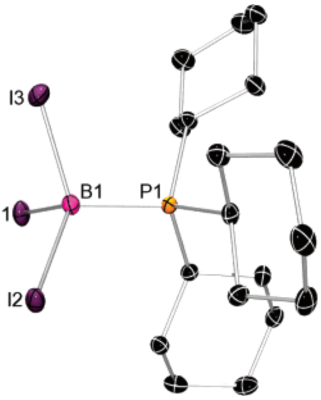


Figure 3. Molecular structure of **1**. Thermal ellipsoids at 50% probability level. Hydrogen atoms and half a molecule of C_6H_6 are omitted for clarity. Selected bond lengths (Å): P1−B1 1.972(3), B1−I1 2.249(3), B1−I2 2.236(3), B1−I3 2.237(3).

2.6707(17) Å (trans to PCy_3) and 2.597(2) Å (trans to I).[22] The Pt−P bond lengths in **3** (Pt1−P1 = 2.267(2) Å, Pt2−P2 = 2.268(2) Å) are 9 pm shorter than those in the monomeric complex **2** (Pt1−P1 = 2.3524(15) Å, Pt1−P2 = 2.3579(15) Å) but comparable to other I-bridged complexes, for example, $[Pt_2(\mu\text{-}I)_2dppm][BF_4]_2$ (2.243(2) and 2.240(2) Å)[21] or $[Pt_2(\mu\text{-}I)_2I_2(PCy_3)_2]$ (2.327(5) Å).[22] The Pt−B bonds with separations of 2.002(11) and 1.971(12) Å are longer than those in **2** but still in the range of the Pt−boryl distances.

In addition, the phosphine borane adduct **1**, which in contrast to to the aforementioned procedure can be directly obtained from the reaction of Cy_3P and BI_3, was subjected to a single-crystal X-ray analysis (Figure 3).

The arrangement around the boron is tetrahedral, and the phosphine adopts a staggered conformation with respect to the iodine atoms. The P−B distance of 1.972(3) Å is slightly elongated in comparison to the one found in $[(H_2C{=}CH)_3P{-}BI_3]$ (1.944(4) Å)[23] or $[Me_3P{-}BI_3]$ (1.918(15) Å),[24] which is probably induced by the greater sterical demands of the cyclohexyl groups. The other structural parameters of **1** are similar to those of the other BI_3 phosphine adducts.[23,24] The average B−I bond lengths for the adducts are 2.249(12) Å for $[Me_3P{-}BI_3]$, 2.229(4) Å for $[(H_2C{=}CH)_3P{-}BI_3]$, and 2.241(3) Å for **1**.

Conclusion

In conclusion, we prepared and fully characterized the first diiodoboryl complex *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$, which is characterized by a very short Pt−B distance and the strong trans influence of the boryl group. Furthermore, *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$ was converted into the iodine-bridged diiodoboryl complex *trans*-$[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ by the addition of BI_3. This dimerization is reversible, and the reaction with PCy_3 affords *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$.

Experimental Section

General Considerations. All manipulations were conducted under an atmosphere of dry argon or in vacuo using standard Schlenk-line or glovebox techniques. Benzene, toluene, and hexane were purified by distillation from Na/K alloy under dry argon and stored over molecular sieves in the glovebox. C_6D_6 and C_7D_8 were degassed by three freeze−pump−thaw cycles and stored over molecular sieves in the glovebox. NMR spectra were recorded 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). $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and 85% H_3PO_4, respectively. Microanalyses for C and H were performed on a Elementar Vario MICRO cube instrument. $[Pt(PCy_3)_2]$ and BI_3 were synthesized according to previously published procedures.

$[Cy_3P{-}BI_3]$ (**1**): $[Pt(PCy_3)_2]$ (200 mg, 0.265 mmol) and BI_3 (260 mg, 0.794 mmol) were dissolved in toluene (4.0 mL). The mixture immediately turned brown. After 3 h at 55 °C, yellow crystalline material had been formed, which was separated from the brown solution via cannula and dried in vacuo, yielding 70 mg (39%) of pure colorless $[Cy_3P{-}BI_3]$. Alternatively, equimolar amounts of PCy_3 and BI_3 were dissolved in C_6H_6, yielding **1**. Single crystals were obtained by the slow evaporation of the solvent.

^1H NMR (500.1 MHz, C_6D_6, 23 °C): δ 2.89 (m, 3H, Cy), 2.27 (m, 6H, Cy), 1.57 (m, 12H, Cy), 1.46 (m, 3H, Cy), 1.11 (m, 6H, Cy), 0.94 (m, 3H, Cy). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 23 °C): δ 35.5 (d, $^1J_{C-P} = 31$ Hz, C^1, Cy), 28.5 (d, $^3J_{C-P} = 4$ Hz, $C^{3,5}$, Cy), 27.2 (d, $^2J_{C-P} = 10$ Hz, $C^{2,6}$, Cy), 25.8 (d, $^4J_{C-P} = 1$ Hz, C^4, Cy). $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6, 23 °C): δ −74.1 (d, $^1J_{B-P} = 117$ Hz). $^{31}P\{^1H\}$ NMR (202.4 MHz, C_6D_6, 22 °C): δ −26.6 (q, $^1J_{P-B} = 117$ Hz). Elemental Anal. Calcd for $C_{18}H_{36}BI_3P$: C 32.17, H 4.95. Found: C 32.85, H 5.13.

trans-$[(Cy_3P)_2Pt(I)(BI_2)]$ (**2**): A pale yellow solution of $[Pt(PCy_3)_2]$ (100 mg, 0.132 mmol) in C_6H_6 (0.6 mL) was added to a colorless solution of BI_3 (52 mg, 0.132 mmol) in C_6H_6 (0.4 mL). The mixture immediately turned red-brown, and after 15 min, a white, fine solid precipitated. The next day hexane (1 mL) was added to increase the amount of the precipitate. The solid was separated and washed with hexane (2 × 0.5 mL), yielding 62 mg (41%) of pure *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$. Single crystals were obtained by slow evaporation of the solvent from a benzene solution. Alternatively, a stoichiometric amount of PCy_3 (4 mg, 0.014 mmol) was added to a solution of $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ (11 mg, 0.007 mmol) in benzene. Multinuclear NMR data immediately showed complete conversion of the starting materials to t*rans*-$[(Cy_3P)_2Pt(I)(BI_2)]$.

^1H NMR (500.1 MHz, C_6D_6, 24 °C): δ 2.86 (m, 6H, Cy), 2.15 (m, 12H, Cy), 1.82−1.70 (m, 30H, Cy), 1.30 (m, 18H, Cy). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 24 °C): δ 36.7 (vt, $N = |^1J_{C-P} + {}^3J_{C-P}| = 28$ Hz, C^1, Cy), 31.0 (s, $C^{3,5}$, Cy), 27.6 (vt, $N = |^2J_{C-P} + {}^4J_{C-P}| = 12$ Hz, $C^{2,6}$, Cy), 26.6 (s, C^4, Cy). $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6, 24 °C): δ 31.0 (br s). $^{31}P\{^1H\}$ NMR (202.4 MHz, C_6D_6, 24 °C): δ 10.3 ppm (s, $^1J_{P-Pt} = 2737$ Hz). Elemental Anal. Calcd for $C_{36}H_{66}B_2I_6P_2Pt{\cdot}0.5(C_6H_6)$: C 39.48, H 5.86. Found: C 38.94, H 5.69.

$[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ (**3**): $[Pt(PCy_3)_2]$ (205 mg, 0.271 mmol) and BI_3 (228 mg, 0.582 mmol) were placed in a Schlenk tube and dissolved in C_6H_6 (2.0 mL). The mixture immediately turned red-brown and a fine white solid precipitated. After 3 h at 55 °C, yellow crystalline material had been formed, which was separated from the brown solution via a cannula and dried in vacuo. The solid was washed 17 times with benzene (0.3 mL), yielding 102 mg

---

[22] Béni, Z.; Ros, R.; Tassan, A.; Scopelliti, R.; Roulet, R. *Dalton Trans.* **2005**, 315−325.

[23] Monkowius, U.; Nogai, S.; Schmidbaur, H. *Dalton Trans.* **2003**, 987−991.

[24] (a) Denniston, M. L.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1461−1464. (b) Black, D. L.; Taylor, R. C. *Acta Crystallogr., Sect. B* **1975**, *B31* (4), 1116−1120.

(43%) of pure beige $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$. Single crystals were obtained by the slow evaporation of the solvent from a benzene solution. Alternatively, the reaction of equimolar amounts of BI_3 (5 mg, 0.013 mmol) and *trans*-$[(Cy_3P)_2Pt(I)(BI_2)]$ (15 mg, 0.013 mmol) in benzene led to $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$. After 1 h at 60 °C, NMR spectra showed the complete conversion of the starting materials and the formation of the products $[(Cy_3P)(I_2B)Pt(\mu\text{-}I)]_2$ and $[Cy_3P-BI_3]$.

^1H NMR (500.1 MHz, C_7D_8, 22 °C): δ 2.25−2.10 (m, 18H, Cy), 1.78−1.58 (m, 30H, Cy), 1.28−1.11 (m, 18H, Cy). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_7D_8, 23 °C): δ 37.4 (d, $^1J_{C-P} = 30$ Hz, C^1, Cy), 30.7 (s, $C^{3,5}$, Cy), 27.6 (d, $^2J_{C-P} = 12$ Hz, $C^{2,6}$, Cy), 26.5 (s, C^4, Cy). $^{11}B\{^1H\}$ NMR (160.5 MHz, C_7D_8, 22 °C): no signal could be detected, due to the poor solubility of the compound. $^{31}P\{^1H\}$ NMR (202.4 MHz, C_7D_8, 22 °C): δ 15.8 (s, $^1J_{P-Pt} = 4460$ Hz). Elemental Anal. Calcd for $C_{36}H_{66}B_2I_6P_2Pt \cdot C_6H_6$: C 27.84, H 4.00. Found: C 28.03, H 4.03.

Crystal-Structure Determination. The crystal data of **1**−**3** were collected at a Bruker X8 APEX diffractometer with a 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 they were included in structure−factor calculations.

Crystal data for **1**: $C_{18}H_{33}BI_3P \cdot {}^1/_2(C_6H_6)$, $M_r = 710.98$, colorless block, $0.18 \times 0.12 \times 0.09$ mm^3, triclinic space group $P\bar{1}$, $a =$ 8.2530(2) Å, $b = 11.9107(3)$ Å, $c = 13.6448(3)$ Å, $\alpha = 108.6880(10)°$, $\beta = 95.8110(10)°$, $\gamma = 90.8790(10)°$, $V = 1262.40(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.870$ g·cm^{-3}, $\mu = 3.782$ mm^{-1}, $F(000) = 682$, $T = 100(2)$ K, $R_1 = 0.0207$, $R_2 = 0.0548$, 5032 independent reflections [$2\theta \leq 52.54°$], and 232 parameters.

Crystal data for **2**: $C_{36}H_{66}BI_3P_2Pt \cdot {}^1/_2(C_6H_6)$, $M_r = 1186.48$, yellow plate, $0.08 \times 0.21 \times 0.38$ mm^3, monoclinic space group C_2/c, $a = 53.108(6)$ Å, $b = 10.3619(13)$ Å, $c = 38.802(5)$ Å, $\beta = 126.230(4)°$, $V = 17224(4)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.830$ g·cm^{-3}, $\mu = 5.509$ mm^{-1}, $F(000) = 9200$, $T = 100(2)$ K, $R_1 = 0.0792$, $R_2 = 0.1296$, 25577 independent reflections [$2\theta \leq 62.06°$], and 829 parameters.

Crystal data for **3**: $C_{36}H_{66}B_2I_6P_2Pt_2 \cdot (C_6H_6)$, $M_r = 1812.14$, colorless needle, $0.25 \times 0.04 \times 0.03$ mm^3, monoclinic space group $P2_1/c$, $a = 17.6997(14)$ Å, $b = 19.2051(15)$ Å, $c = 16.9665(13)$ Å, $\beta = 114.661(2)°$, $V = 5241.3(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.296$ g·cm^{-3}, $\mu = 8.955$ mm^{-1}, $F(000) = 3352$, $T = 173(2)$ K, $R_1 = 0.0551$, $R_2 = 0.0974$, 10387 independent reflections [$2\theta \leq 52.24°$], and 487 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 649528−649530. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. This work was supported by the DFG.

IC7011028