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Ionic-Type Reactivity of 1,3-Dibora-2,4-diphosphoniocyclobutane-1,3-diyls: Regio- and Stereoselective Addition of Hydracids

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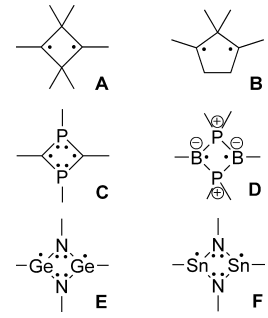
Abstract: Hydrogen chloride and trifluoromethane sulfonic acid readily add to the symmetrically substituted 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl (**1**) and unsymmetrically substituted 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane (**3**) under mild conditions, substantiating some formal analogies between the PBPB diradicaloids **D** and alkenes. X-ray diffraction analyses carried out on all the resulting 1,3-diborata-2,4-diphosphoniocyclobutanes (**2**, **4**−**6**) revealed that the reactions proceed with complete stereo- and regio-selectivity, and that an unusual *t*-Bu → *i*-Bu isomerization can occur at boron. DFT calculations shed more light on the factors controlling the regioselectivity of the additions, its concerted versus stepwise character, and support an original two-step mechanism for the *t*-Bu → *i*-Bu isomerization, involving a carbocationic σ-borane adduct as a key intermediate.

Introduction

Due to their peculiar electronic structure, 1,3-diradicals have attracted increasing interest over the last 20 years.[1,2] The archetypal systems, namely cyclobutane-1,3-diyls **A** and cyclopentane-1,3-diyls **B** have been characterized spectroscopically, both in the triplet[3] and singlet[4] ground states, and are short-living species (Chart 1). In contrast, thanks to the unique properties of heteroelements, singlet 1,3-diradicaloids (**C**−**F**)[5−11] are stable at room temperature, and have recently been isolated as crystalline compounds.

Chart 1



The electronic structure of compounds **A**−**D** has been thoroughly investigated by computational methods.[12,13] The catenation of all these diradicals via covalent linkers has been achieved, providing first insights into the factors influencing the "communication" between the diradical sites.[5m,6d,g,14] Examples of intramolecular rearrangements of **A**−**D**,[5b,c,6c,e,f,15] especially ring closure, 1,2-shift reactions, and valence isomerizations that include bond-stretching isomerizations have been reported. Moreover, although the instability of all-carbon diradicals **A** and **B** almost totally precludes intermolecular reactions,[4b,c,e] an extremely rich intermolecular reactivity has been observed from 2,4-diphosphacyclobutane-1,3-diyls **C**,

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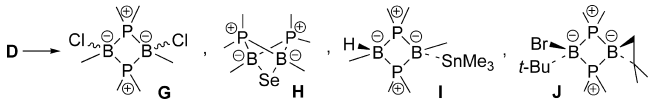
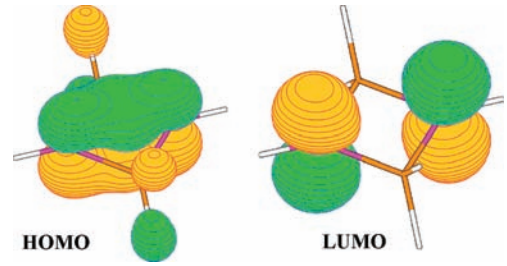
Chart 2



giving access to a variety of unusual phosphorus-containing heterocycles.[5d,e,g−i,k,l] So far, the intermolecular reactivity of 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls **D** has been poorly explored. Oxidation reactions have been reported with $CDCl_3/Cl_2$ and Se/PhSeSePh, leading to the *cis*/*trans*-dichloro and selenium adducts **G** and **H**, respectively. In addition, the spontaneous formation of the 1,3-diborata-2,4-diphosphoniocyclobutanes **I** and **J** upon reaction with trimethyltin hydride and bromotrichloromethane provided convincing evidence for radical-type behavior of **D** (Chart 2).[6b]

Interestingly, in contrast to 2,4-diphosphacyclobutane-1,3-diyls **C**, but similarly to cycloalkane-1,3-diyls **A** and **B**, the frontier orbitals of 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls **D** are associated with in-phase (HOMO) and out-of-phase (LUMO) combinations of $2p_{(B)}$ orbitals, in line with some through-space transannular π-bonding (Chart 3).[6a,13] This suggests that some analogy could be formally drawn between PBPB systems **D** and alkenes, although in contrast with the latter no BB σ-bond is present. This prompted us to investigate the chemical behavior of diradicaloids **D** toward hydracids, and we report here the first experimental and computational evidence of ionic-type reactivity for these PBPB systems.

Chart 3



Results and Discussion

Reaction of PBPB Systems 1 and 3 with HCl. The symmetrically substituted 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**[6a] was treated with 1 equiv of hydrogen chloride (2 M solution in diethyl ether) in toluene at −78 °C. Within 5 min, the solution turned from intense yellow to colorless, indicating the complete consumption of **1**. According to ^{1}H NMR spectroscopy, a new compound **2** was formed in >80% yield (Scheme 1). The mass spectrum [EI, m/z = 406 (M^+)]

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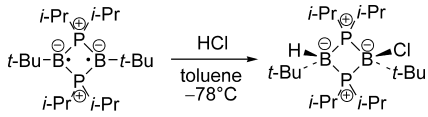
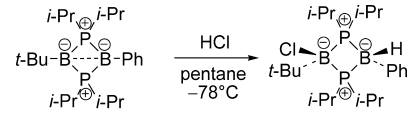
Scheme 1



1 **2**

Scheme 2



3 **4**

was consistent with the expected 1:1 addition product, and the two signals observed at δ 5.6 and −15.0 ppm in the ^{11}B NMR spectrum indicate the presence of two inequivalent anionic tetracoordinate boron centers. Besides the typical signals associated with the *i*-Pr groups at phosphorus and the *t*-Bu groups at boron, the ^{1}H NMR spectrum exhibits a broad signal attributable to a BH proton at δ 3.06 ppm. Colorless crystals (54% yield, mp = 96 °C) were obtained from a saturated toluene solution at low temperature, and the molecular structure of **2** was definitely confirmed by X-ray crystallography (Figure 1, Table 2 in Experimental Section). Upon addition of HCl, the BPBP four-membered ring is retained, but is noticeably distorted from planarity (the interflap angle between the two PBB units decreases from 180° in **1** to 154.5° in **2**). The cancellation of both through-space and through-bond BB interactions is accompanied by a substantial elongation of the PB bonds (from 1.89 Å in **1** to 1.99−2.05 Å in **2**) and BB distance (from 2.57 Å in **1** to 2.82−2.83 Å in **2**). The hydrogen and chlorine atoms at the boron centers are disordered (the positions for the hydrogen atom at boron were located and refined without constraint), but the assignment of the *cis* relationship between the two incoming atoms can be done without doubt. The formation of **2** corresponds to the 1,3-addition of HCl across the formal transannular π(BB) bond of the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**. The complete stereoselectivity in favor of the cis addition strongly suggests a concerted process.

We then envisioned to probe the regioselectivity of the addition reaction, and thus looked for a unsymmetrically substituted PBPB substrate. Since, to date, the cyclobutane-1,3-diyl ground-state structure has only been found for symmetrically substituted PBPB compounds,[6a,c,e] the study was carried out on the unsymmetrically substituted bicyclo[1.1.0]butane **3**. Although this compound has a bicyclic ground-state structure, it rapidly inverts in solution at room temperature via the corresponding cyclobutane-1,3-diyl.[16] In addition, similar chemical reactivity has been observed for PBPB compounds adopting cyclobutane-1,3-diyl and bicyclo[1.1.0]butane ground-state structures, including for the radical addition of $HSnMe_3$.[17]

Upon addition of hydrogen chloride in pentane, the deep red color characteristic of the unsymmetrically substituted 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3**[6g] disappeared within a few minutes, and a new compound **4** was obtained as a single isomer in >90% yield, according to ^{1}H NMR spectroscopy (Scheme 2). The chemical formula of **4** was supported by mass spectrometry [ESI, m/z = 449 (M + Na^+)], and diagnostic signals were observed at δ 6.7 and −18.4 ppm in the ^{11}B NMR, and δ 3.39 ppm in the ^{1}H NMR spectrum (BH proton). X-ray quality crystals were obtained from a saturated pentane solution at low temperature (37% yield, mp = 141 °C) (Figure 2). The hydrogen atom at boron was located and refined without constraint. Here also, the addition of HCl induces some folding of the PBPB four-membered ring (the interflap angle between the two PBB units is 150.3°), and the two incoming atoms are in cis relationship. The chlorine atom is bonded to the *t*-Bu-substituted boron, while the hydrogen atom is linked to the Ph-substituted boron center. Thus, the addition of HCl to the unsymmetrically substituted 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3** proceeds with complete regioselectivity and cis-stereoselectivity. Surprisingly, the chlorine atom adds to the more sterically shielded boron center rather than to the Ph-stabilized one, leading selectively to product **4**.

Theoretical Study of the Addition of HCl to 3. To gain more insight into the factors controlling the stereoselectivity and regioselectivity of the addition of HCl to **3**, density functional theory (DFT) calculations were carried out. The actual PBPB

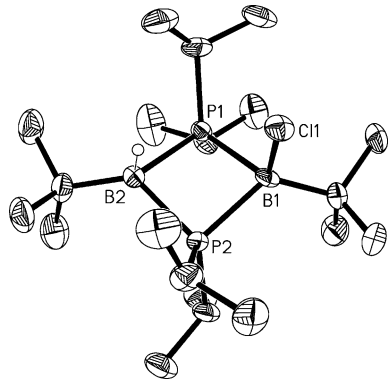


Figure 1. Molecular view of compound **2** in the solid state, with hydrogen atoms omitted except at B2. Thermal ellipsoids projected at the 50% probability level. For clarity, only one of the two independent molecules present in the asymmetric unit is shown. Selected bonds distances (Å) and angles (deg): P1−B1, 2.050(5); P1−B2, 1.994(5); P2−B1, 2.030(5); P2−B2, 1.990(5); P1−B1−P2, 86.8(2); B1−P2−B2, 89.1(2); P2−B2−P1, 89.5(2); B2−P1−B1, 88.4(2).

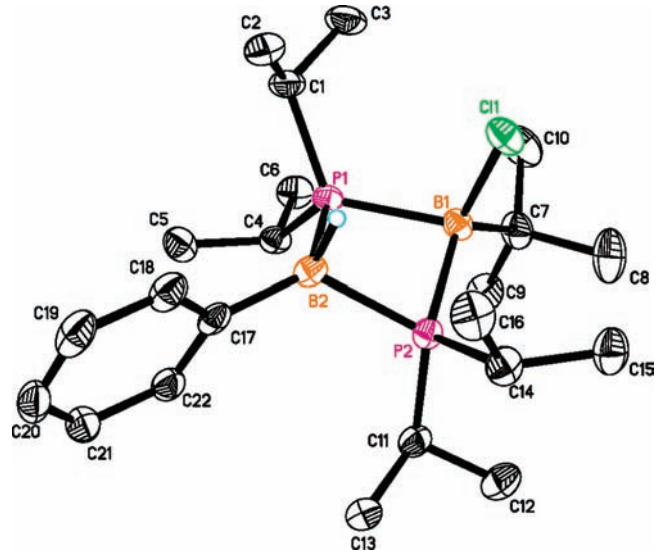


Figure 2. Molecular view of compound **4** in the solid state, with hydrogen atoms omitted except at B2. Thermal ellipsoids projected at the 50% probability level. For clarity, only one independent molecule of the unit cell is shown. Selected bonds distances (Å) and angles (deg): P1−B1, 2.036(3); P1−B2, 1.978(2); P2−B1, 2.048(2); P2−B2, 1.979(2); B1−Cl1, 1.901(3); P1−B1−P2, 86.4(1); B1−P2−B2, 87.7(1); P2−B2−P1, 89.9(1); B2−P1−B1, 88.0(1).

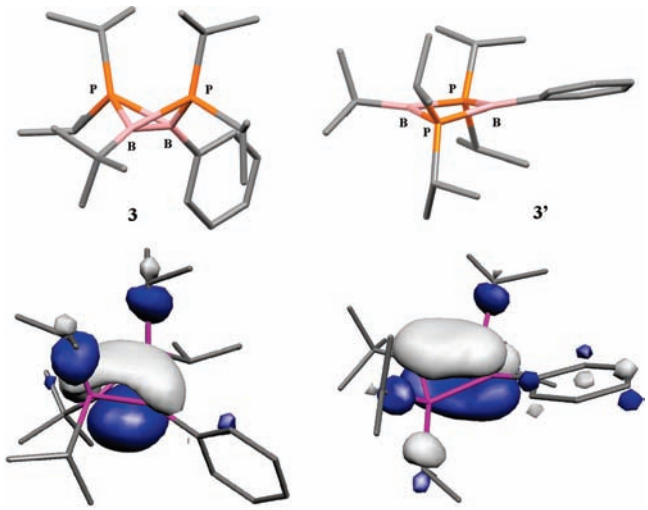


Figure 3. Optimized geometries and Kohn−Sham representations of the HOMO orbitals for the 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3** and the corresponding 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl structure **3′**.

Table 1. Mulliken Charges Computed for the 1,3-Dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3** and the Corresponding 1,3-Dibora-2,4-diphosphoniocyclobutane-1,3-diyl **3′**[18]

	Mulliken charges	
	B(*t*-Bu)	B(Ph)
3	0.30	0.18
3′	0.18	−0.01

system was considered in order to reliably take into account substituent effects. Accordingly, the geometric parameters of the 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3** computed at the B3PW91/SDD(P,Cl),6-31G**(B,C,H) level of theory (BB 1.836 Å, PB 1.91−1.94 Å, fold angle 117.4°) nicely reproduced those measured experimentally for the related system featuring a β-naphthyl in place of phenyl group at boron (BB 1.884 Å, PB 1.85−1.91 Å, fold angle 121.5°).[6g] The corresponding cyclobutane-1,3-diyl structure **3′** (BB 2.569 Å, PB 1.91−1.92 Å, fold angle 165.8°) was found to be the transition state for the inversion of the bicyclo[1.1.0]butane **3**, but only 9.7 kcal/mol higher in energy.

The HOMO orbitals of **3** and **3′** correspond formally to π-type interaction between the two boron centers, involving pure 2p(B) orbitals in **3′** and slightly hybridized orbitals in **3** (Figure 3). Despite the dissymmetric substitution pattern, the HOMOs of **3** and **3′** are both almost equally distributed over the two boron centers. It seems thus unlikely that orbital factors are responsible for the regioselectivity upon the addition of HCl to **3**. We then considered electrostatic effects and noticed a small dissymmetry in the atomic charges of the two boron centers. In both forms **3** and **3′**, a slightly more positive atomic charge is predicted for the B(*t*-Bu) center compared to the B(Ph) one (Table 1), in agreement with the selective addition of Cl at B(*t*-Bu) and H at B(Ph). However, the difference in the atomic charges remains fairly small to claim with certainty that the reaction proceeds under charge control.

The potential energy surface for the addition of HCl to **3** was then scrutinized (Figure 4). The formation of the 1,3-diborata-2,4-diphosphoniocyclobutane **4** was predicted to be highly exothermic (ΔG −48.4 kcal/mol), and a transition state $\mathbf{TS_{3\rightarrow 4}}$, connecting both compounds, was located 8.7 kcal/mol higher in energy than **3**. This profile is in good agreement with the fast addition observed at low temperature, and the structure of $\mathbf{TS_{3\rightarrow 4}}$ supports a concerted but strongly asynchronous pathway for the addition of HCl to **3**. The HCl molecule approaches almost perpendicularly to the PBPB core of **3**, with a close B(Ph)/H contact (the corresponding distance is 1.55 Å in $\mathbf{TS_{3\rightarrow 4}}$, as compared with 1.21 Å in the addition product **4**), substantial elongation of the H−Cl bond (from 1.29 Å in the free form to 1.59 Å in $\mathbf{TS_{3\rightarrow 4}}$), but virtually no B(*t*-Bu)/Cl interaction (the corresponding distance is 4.72 Å in $\mathbf{TS_{3\rightarrow 4}}$, as compared with 3.6 Å for the sum of van der Waals radii[19]). The regioisomeric adduct **4′** [with the chlorine atom bonded to B(*t*-Bu) and the hydrogen atom linked to B(Ph)] was found 2.4 kcal/mol higher in energy than **4**, while the related transition state $\mathbf{TS_{3\rightarrow 4'}}$ was found 0.6 kcal/mol lower in energy than $\mathbf{TS_{3\rightarrow 4}}$. This suggests that the regioselective formation of **4** is probably thermodynamically rather than kinetically controlled, but the small energetic difference predicted between the two pathways prevents definitive conclusion.

Reaction of PBPB Systems 1 and 3 with HOTf. To investigate the influence of steric factors on the stereo- and regioselectivities observed in the reactions with HCl, compound **3** was then reacted with trifluoromethane sulfonic acid. One equivalent of HOTf was added at −78 °C to a pentane solution of the 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3**. The reaction proceeded more slowly than with HCl, as apparent from the progressive discoloration of the reaction mixture over 2 h at room temperature. Here again, a single product **5** was formed (Scheme 3). The solubility of **5** in pentane suggested a covalent rather than ionic structure. This contrasts with the formation of the diphosphino-carbocation **K** observed by Niecke et al. upon reaction of HOTf with a 2,4-diphosphacyclobutane-1,3-diyl **C** [Mes* = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$].[5i] Compound **5** exhibits two ^{11}B NMR signals in the range typical for tetracoordinated anionic boron centers (δ 4.9 and −18.3 ppm) and a broad ^{1}H NMR signal at δ 3.85 ppm attributable to a BH proton. In addition, the resonance observed at δ −78.1 ppm in the ^{19}F NMR spectrum is consistent with the presence of a trifluoromethane sulfonate moiety. The formulation of **5** as a 1:1 adduct between HOTf and **3** was further supported by mass spectrometry [EI, m/z = 540 (M^+)], and definitely confirmed by X-ray diffraction analysis (20% isolated yield, mp = 155 °C, Figure 5). The hydrogen atom (located and refined without constraint) and trifluoromethane sulfonate group are bonded to the two boron centers, in a cis relationship relative to the PBPB core. The BO bond length (1.54 Å) is in the same range as those reported for the few structurally authenticated tetracoordinated boron derivatives featuring a covalently bonded trifluoromethane sulfonate group (1.50−1.63 Å).[20] Surprisingly, the hydrogen atom is linked to the B(*t*-Bu) center and the trifluoromethane sulfonate moiety is bonded to the B(Ph) boron center in **5**. Thus, a complete inversion of regioselectivity is observed upon addition

(16) All 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butanes have been shown by NMR to invert readily in solution at room temperature (the axial and equatorial phosphorus substituents are magnetically equivalent).
(17) Scheschkewitz, D.; Amii, H.; Vranicar, L.; Bourissou, D.; Bertrand, G. Unpublished results.
(18) Similarly, NBO calculations predicted atomic charges at B(t-Bu) higher by about 0.1 unit than those at B(Ph) for both **3** and **3′** (see Supporting Information).
(19) Batsanov, S. S. *Inorg. Mater.* **2001**, *37*, 871–885.

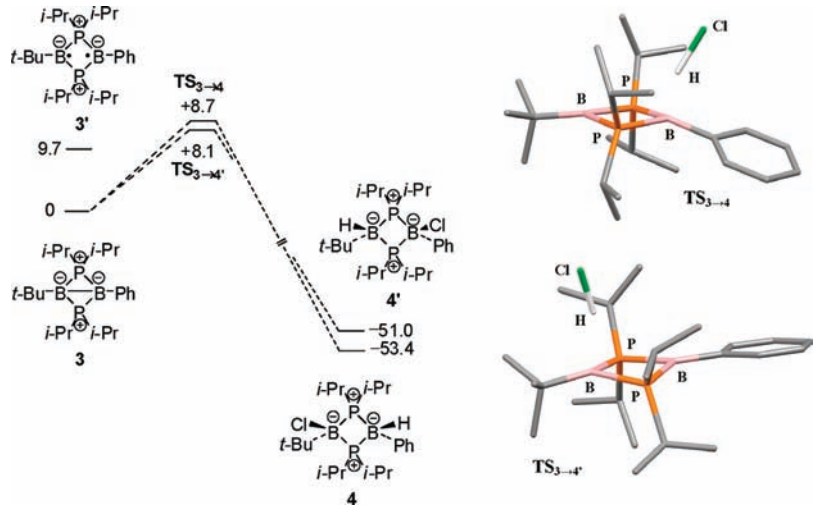
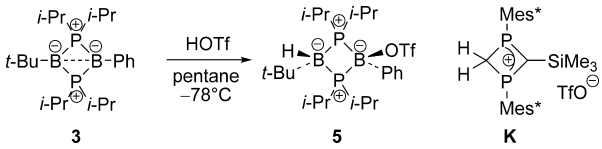


Figure 4. Energy profiles computed at the B3PW91/SDD(P,Cl),6-31G**(B,C,H) level of theory (free energies G at 25 °C including ZPE correction in kcal/mol) for the addition of HCl to the 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3**.

Scheme 3



of HCl and HOTf to **3**, suggesting that subtle steric and electronic effects dramatically influence the outcome of the reaction. In this respect, at this stage, the selective formation of **5** was tentatively attributed to the extreme steric protection of the B(*t*-Bu) boron center that may prevent the addition of the trifluoromethane sulfonate group.

To further estimate the influence of the steric effects, the addition of HOTf to the PBPB diradicaloid **1**, featuring *t*-Bu groups at both boron centers, was studied. The reaction was

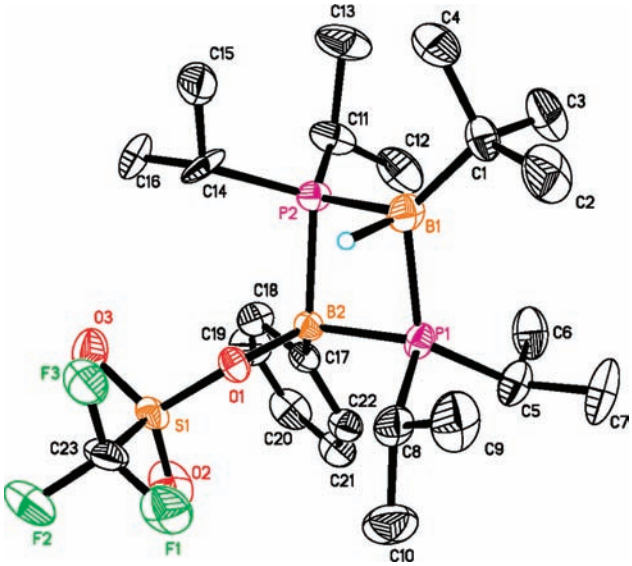
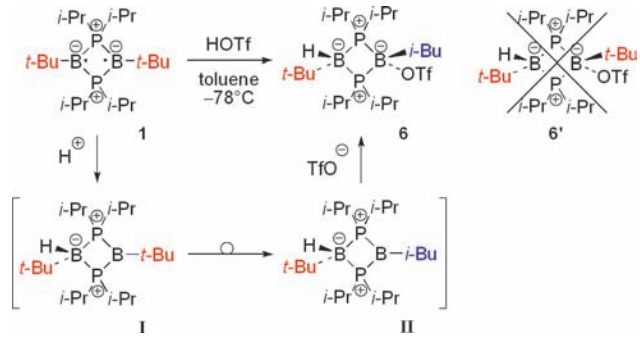


Figure 5. Molecular view of compound **5** in the solid state, with solvate molecules and hydrogen atoms omitted except at B1. Thermal ellipsoids projected at the 50% probability level. Selected bonds distances (Å) and angles (deg): P1−B1, 2.000(6); P1−B2, 2.041(3); P2−B1, 1.995(4); P2−B2, 2.031(5); B2−O1, 1.541(5); P1−B1−P2, 90.4(2); B1−P2−B2, 89.7(2); P2−B2−P1, 88.2(2); B2−P1−B1, 89.2(2).

Scheme 4



complete after 1 h at −78 °C in toluene, as apparent from the disappearance of the characteristic yellow color of the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**. The NMR (^{11}B, δ 6.2 and −17.9 ppm; ^{1}H, δ 2.57 ppm; and ^{19}F, δ −76.7 ppm) and mass spectrometry [EI, m/z = 520 (M^+)] data for the resulting product **6** were consistent with the 1,3-addition of HOTf (Scheme 4). To unambiguously establish the structure of compound **6**, crystals were grown from a saturated pentane solution at low temperature (45% yield, mp 105 °C) and an X-ray diffraction study was carried out (Figure 6). Accordingly, addition of HOTf had indeed occurred on the formal transannular π(BB) bond of **1**. But remarkably, the hydrogen atom (located and refined without constraint) and trifluoromethane sulfonate group are in a *trans* relationship relative to the PBPB core. This result suggests that, in this case, the addition does not proceed via a concerted but rather a stepwise mechanism. Moreover, in contrast to **1**, the substituents at the two boron centers are no longer identical in **6**; the TfO-substituted boron

(20) (a) Müller, M.; Eversheim, E.; Englert, U.; Boese, R.; Paetzold, P. *Chem. Ber.* **1995**, *128*, 99–103. (b) Imamoto, T.; Asakura, K.; Tsuruta, H.; Kishikawa, K.; Yamaguchi, K. *Tetrahedron Lett.* **1996**, *37*, 503–504. (c) Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I.; McWilliams, A. R.; Guzei, I. A.; Yap, G. P. A. *Chem.—Eur. J.* **1998**, *4*, 1489–1503. (d) Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857–867. (e) Clemente, D. A. *Tetrahedron* **2003**, *59*, 8445–8455. (f) Forster, T. D.; Krahulic, K. E.; Tuononen, H. M.; McDonald, R.; Parvez, M.; Roesler, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6356–6359. (g) Vidovic, D.; Findlater, M.; Cowley, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 8436–8437. (h) Hudnall, T. W.; Gabbaï, F. P. *Chem. Commun.* **2008**, 4596–4597.

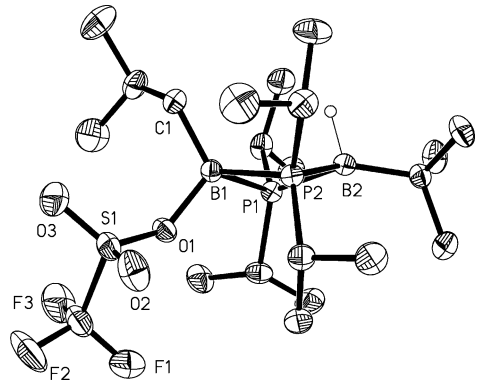


Figure 6. Molecular view of compound **6** in the solid state, with hydrogen atoms omitted except at B2. Thermal ellipsoids projected at the 50% probability level. Selected bonds distances (Å) and angles (deg): P1−B1, 2.032(3); P1−B2, 1.986(2); P2−B1, 2.037(2); P2−B2, 1.974(3); B1−O1, 1.550(4); P1−B1−P2, 87.3(1); B1−P2−B2, 88.0(1); P2−B2−P1, 90.3(1); B2−P1−B1, 87.8(1).

atom features an *i*-butyl instead of a *t*-butyl group. The rearrangement of *t*-Bu into *i*-Bu substituent at boron is rare but not unprecedented. It has been observed during the preparation or distillation of sterically hindered *t*-butyl boranes.[21] The selective *t*-Bu → *i*-Bu isomerization observed upon addition of HOTf to **1** parallels, to some extent, the reverse regioselectivity noticed upon additions of HCl and HOTf to **3**, and thereby further supports the hypothesis that a *t*-Bu group at boron prevents sterically the addition of the trifluoromethane sulfonate group (that would have led to **6′**).

As mentioned above, the trans arrangement of the hydrogen atom and trifluoromethane sulfonate group in **6** indicates that HOTf adds stepwise to the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**. Most likely, the reaction starts by protonation of one of the electron-rich boron center of **1** leading to the cationic intermediate **I** (Scheme 4). *t*-Bu → *i*-Bu isomerization at the tricoordinate boron atom would then give compound **II**. Lastly, addition of the trifluoromethane sulfonate to the sterically accessible and planar B(*i*-Bu) center would finally afford the trans product **6** that probably suffers from less steric congestion than its cis isomer.[22]

Theoretical Study of the *t*-Bu → *i*-Bu Isomerization upon Addition of HOTf to 1. To shed some light on the key isomerization step **I** → **II**, DFT calculations were carried out.[23] The two isomeric structures were located as energy minima on the potential energy surface. In both cases, the incoming proton is linked to a single boron center, any conceivable H-bridging structure being disfavored by the rather large distance between the two boron atoms. The optimized geometry for compound **I** (Figure 7) suggests some secondary interaction between the *t*-Bu substituent and the tricoordinate boron center: short H···B contact of 1.818 Å, slight elongation of the corresponding C−H bond (1.126 vs 1.090 Å), and acute BCC bond angle (79.2°). This interaction probably compensates to some extent the high electron deficiency of the bis-onio borane moiety of **I**. This is reminiscent to the contribution of hyperconjugation or "agostic" bonding in B(*t*-Bu)$_3$, as discussed recently by Downs, Parsons et al. on the basis of X-ray diffraction and computational data.[24] The *t*-Bu → *i*-Bu isomerization is predicted to be favored thermodynamically, cation **II** being more stable than **I** by 10.7 kcal/mol.

The potential energy surface (PES) was then scrutinized in order to find a low energy pathway between **I** and **II**. We first located the transition state $\mathbf{TS_I}$ associated with the transfer of a hydrogen atom from one methyl group of the *t*-Bu substituent to the tricoordinate boron center. $\mathbf{TS_I}$ was found 12.4 kcal/mol higher in energy than **I** (Figure 8). According to the optimized geometry (Figure 9), it corresponds to an isobutylene π complex. One boron center is formally pentacoordinate.[25] As expected, the boron center is more tightly bonded to the terminal carbon atom (with B-CH_2 and B-CMe_2 distances of 1.841 and 1.915 Å, respectively). The isobutylene fragment retains some double bond character with a CC bond length of 1.389 Å, and a marginal pyramidalization of the two carbon centers (the sum of the bond angles Σ_α equals 354.3° for C*C*Me$_2$ and 357.3° for C*C*H$_2$). Such π olefin/borane complexes have been recognized as key intermediates in hydroboration reactions, but to the best of our knowledge, have not been isolated nor characterized to date.[26−28] $\mathbf{TS_I}$ leads to compound **III**, which is located 7.0 kcal/mol higher in energy than **I**, by slippage of the boron center to the terminal carbon atom. The B-CH_2 bond shortens to 1.819 Å and the C*C*H$_2$ center noticeably pyramidalizes ($\Sigma_\alpha = 347°$). The C*C*Me$_2$ atom remains trigonal planar (359.6°) and no longer interacts with the boron center (the BC distance reaches 2.503 Å). Compound **III** is thus best described as a 1,3-dihydro-1,3-diborata-2,4-diphosphoniocyclobutane featuring a pendant carbocation. Upon rotation around the B-CH_2 bond, another energy minimum **III′** could be located on the PES. It is significantly

(21) For early reports on the rearrangement of *t*-Bu boranes, see:(a) Hennion, G. F.; McCusker, P. A.; Marra, J. V. *J. Am. Chem. Soc.* **1957**, *79*, 5190–5191. (b) Hennion, G. F.; McCusker, P. A.; Marra, J. V. *J. Am. Chem. Soc.* **1958**, *80*, 617–619. (c) Hennion, G. F.; McCusker, P. A.; Marra, J. V. *J. Am. Chem. Soc.* **1958**, *80*, 3481–3482. (d) Hennion, G. F.; McCusker, P. A.; Marra, J. V. *J. Am. Chem. Soc.* **1959**, *81*, 1768. (e) McCusker, P. A.; Marra, J. V.; Hennion, G. F. *J. Am. Chem. Soc.* **1961**, *83*, 1924–1928. (f) Rossi, F. M.; McCusker, P. A.; Hennion, G. F. *J. Org. Chem.* **1967**, *32*, 450–452. (g) Nöth, H.; Taeger, T. *J. Organomet. Chem.* **1977**, *142*, 281–288.

(22) The ionic pathway 1 → I → II → **6** is somewhat reminiscent of the radical mechanism proposed to account for the reaction of **1** with bromotrichloromethane.[6b]

(23) As noted by one reviewer, ion pair contacts may affect the geometric and energetic features of the reaction profile for the *t*-Bu → *i*-Bu isomerization, but this effect could not be taken into consideration here because of prohibitive computational times.

(24) Cowley, A. R.; Downs, A. J.; Marchant, S.; Macrae, V. A.; Taylor, R. A.; Parsons, S. *Organometallics* **2005**, *24*, 5702–5709.

(25) For discussions about the existence and structure of BH_5, see:(a) Tague, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4970–4976. (b) Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 7625–7632. (c) Watts, J. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 825–826. (d) Jursic, B. S. *J. Mol. Struct.* **1999**, *492*, 97–103. (e) Kim, Y.; Kim, J.; Kim, K. H. *J. Phys. Chem. A* **2003**, *107*, 301–305. (f) Schuurman, M. S.; Allen, W. D.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Chem. Phys.* **2005**, *122*, 104302/1–104302/12.

(26) For computational studies of hydroboration, see:(a) Sundberg, K. R.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1979**, *101*, 2863–2869. (b) Nagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536–4537. (c) Wang, X.; Li, Y.; Wu, Y.-D.; Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 2601–2609. (d) Long, L.; Lu, X.; Tian, F.; Zhang, Q. *J. Org. Chem.* **2003**, *68*, 4495–4498. (dd) Oyola, Y.; Singleton, D. A. *J. Am. Chem. Soc.* **2009**, *131*, 3130–3131.

(27) For recent studies suggesting the transient formation of olefin π-complex as key intermediates, see:(a) Scheideman, M.; Shapland, P.; Vedejs, E. *J. Am. Chem. Soc.* **2003**, *125*, 10502–10503. (b) Clay, J. M.; Vedejs, E. *J. Am. Chem. Soc.* **2005**, *127*, 5766–5767. (c) Scheideman, M.; Wang, G.; Vedejs, E. *J. Am. Chem. Soc.* **2008**, *130*, 8669–8676. (d) Wang, G.; Vedejs, E. *Org. Lett.* **2009**, *11*, 1059–1061.

(28) For Van der Waals complexes between alkenes and BF_3, see: Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **1997**, *119*, 10446–10454. Attractive interactions have been recently predicted computationally between 6π-electron rings and BH_3: Kawahara, S.-i.; Tsuzuki, S.; Uchimaru, T. *Chem.—Eur. J.* **2005**, *11*, 4458–4464.

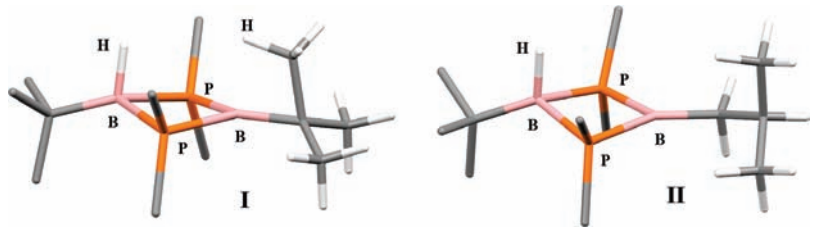


Figure 7. Optimized geometries for **I** and **II**.

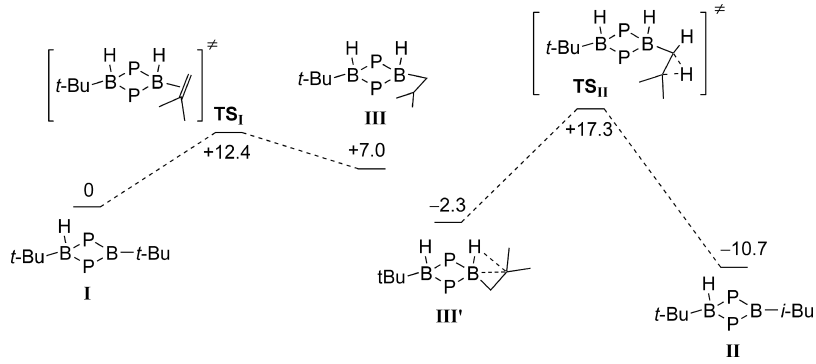


Figure 8. Energy profile computed at the B3PW91/SDD(P,Cl),6-31G**(B,C,H) level of theory (free energies G at 25 °C including ZPE correction in kcal/mol) for the *t*-Bu → *i*-Bu isomerization from **I** to **II** (*i*-Pr substituents at phosphorus and atomic charges omitted for clarity).

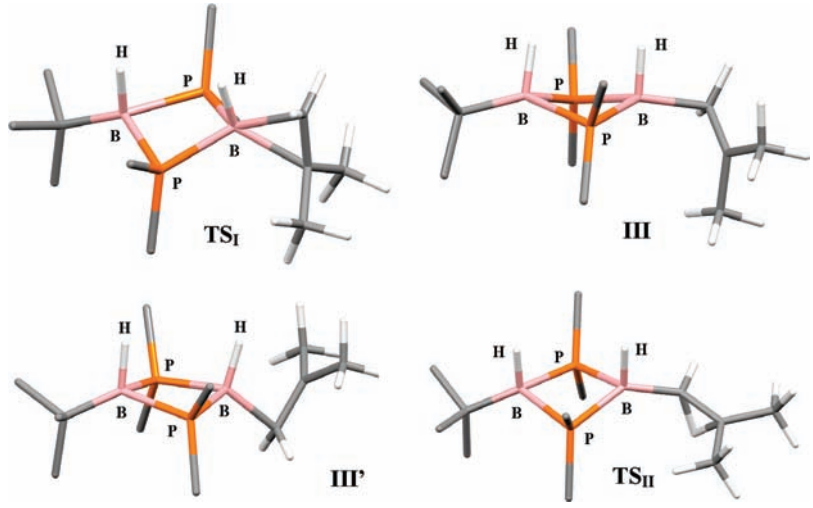


Figure 9. Optimized geometries for $\mathbf{TS_I}$, **III**,**III′**, and $\mathbf{TS_{II}}$.

more stable than **III**, and even 2.3 kcal/mol lower in energy than **I**. In contrast to **III**, compound **III′** retains some B···C(Me_2) interaction [the corresponding distance is 2.107 Å, and the BCC(Me_2) bond angle is rather acute at 83.6°]. A short contact is also observed between the hydrogen atom at boron and the carbocationic center C*C*(Me_2) (2.142 Å). The relationship between the π complex $\mathbf{TS_I}$ and the σ adducts **III**/**III′** is strongly reminiscent to that recently pointed out between the η^2 and η^1 forms of $[Cp_2Zr(alkyl)(alkene)]^+$ complexes (Figure 10).[29]

Quite surprisingly, no transition state could be located for the back transfer of a hydrogen atom from the boron center directly to the C(Me_2) atom. The formation of **II** rather results from a concerted double 1,2-shift of hydrogen from B to C(H_2) and from C(H_2) to C(Me_2). Indeed, transition state $\mathbf{TS_{II}}$ was found to connect directly **III′** and **II**. According to the optimized geometry of $\mathbf{TS_{II}}$, the hydrogen shift from C(H_2) to C(Me_2) is much more advanced than that from B to C(H_2), with a quasi-

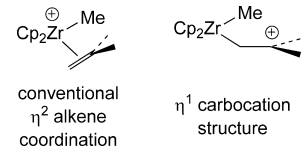


Figure 10. η^2 and η^1 forms for the $[Cp_2Zr(alkyl)(alkene)]^+$ complexes.

symmetrically bridging hydrogen atom between C(H_2) and C(Me_2) (the corresponding CH distances are 1.293 and 1.330 Å, respectively), while the other migrating hydrogen remains exclusively bonded to the boron center (the cleaving BH and forming CH bond lengths are 1.217 and 2.173 Å, respectively). $\mathbf{TS_{II}}$ is located 17.3 kcal/mol higher in energy than **I**.

The activation barrier for the overall process can thus be estimated at about 20 kcal/mol (in the gas phase), in agreement with a rather fast reaction at room temperature in the liquid state. The isomerization of **I** into **II** is predicted to proceed in

two steps: (*i*) transfer of a hydrogen atom from *t*-Bu to boron (formal dehydroboration reaction), and (*ii*) an original double, concerted, 1,2-shift of hydrogen from B to $C(H_2)$ and from $C(H_2)$ to $C(Me_2)$. The high electron deficiency of the tricoordinate boron atom in **I** and **II** probably explains why the transition states $\mathbf{TS_I}$ and $\mathbf{TS_{II}}$ are accessible. In this respect, it is striking to note that the carbocationic structure **III′** is intermediate in stability between the two cationic borane forms **I** and **II**.

Conclusion

HCl and HOTf were found to add readily to the PBPB core of 1,3-dibora-2,4-diphosphonicyclobutane-1,3-diyls **D** under mild conditions. The reactions proceed concertedly or stepwise, but always with complete stereo- and regio-selectivity. X-ray diffraction analyses carried out on all the resulting 1,3-diborata-2,4-diphosphoniocyclobutanes (**2**, **4**−**6**) revealed that the concerted versus stepwise character of the addition is controlled by subtle steric and electronic effects and that the reaction may be accompanied by an unusual *t*-Bu → *i*-Bu isomerization at boron. DFT calculations support an original two-step mechanism for the *t*-Bu → *i*-Bu isomerization involving a carbocationic σ-borane adduct as key intermediate.

These results further illustrate that PBPB diradicaloids **D** combine high thermal stability and versatile reactivity. The addition of hydracids provides the first evidence of ionic-type behavior and substantiates some formal analogy with alkenes, in agreement with the symmetry of the frontier molecular orbitals.

Experimental Section

All reactions were performed using standard Schlenk techniques under an argon atmosphere. ^{31}P, ^{1}H, ^{11}B, ^{19}F and ^{13}C spectra were recorded on Bruker Avance 300 or 400 and AMX500 spectrometers. ^{31}P, ^{1}H, ^{11}B, ^{19}F and ^{13}C chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4, Me_4Si, $FCCl_3$, and $BF_3 \cdot OEt_2$. Toluene was dried under sodium and distilled prior to use, pentane was dried under CaH_2 and distilled prior to use. All organic reagents were obtained from commercial sources and used as received. F_3CSO_3H and HCl (2 M solution in diethyl ether) were purchased from Aldrich Chemicals. The 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**[6a] (*t*-Bu/*t*-Bu) and 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butane **3**[6g] (*t*-Bu/Ph) were prepared according to literature procedures.

Synthesis of 1,3-Diborata-2,4-diphosphoniocyclobutane (2). A 70 μL (0.140 mmol) portion of HCl (2 M in Et_2O) was added at −78 °C to a solution of compound **1** (50 mg, 0.140 mmol) in toluene (2 mL). After the solution was stirred for 5 min at −78 °C, the discoloration was complete. ^{1}H NMR spectroscopy of the crude mixture allowed the observation of the formation of a major compound (>80%). The solution was concentrated and kept in a freezer to yield colorless crystals suitable for X-ray analysis. Yield 29 mg (54%); mp 96 °C. ^{31}P NMR (121 MHz, C_6D_6): δ_{ppm} 12.2 (broad). ^{11}B-NMR (96 MHz, C_6D_6): δ_{ppm} 5.6 (s, *B*Cl), −15.0 (s, *B*H). ^{1}H NMR (300 MHz, C_6D_6): δ_{ppm} 3.06 (broad, 1H, *H*B), 2.19 (m, 4H, PC*H*), 1.47 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.22 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.16 (s, 9H, $C(CH_3)_3$), 1.13 (s, 9H, $C(CH_3)_3$), 1.09 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.05 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$-NMR (75.5 MHz, C_6D_6): δ_{ppm} 35.2 (pseudo-t, $C(CH_3)_3$ $^{3}J_{C,P} = 6.1$ Hz), 31.7 (pseudo-t, $C(CH_3)_3$ $^{3}J_{C,P} = 4.1$ Hz), 26.7 (pseudo-t, P*C*H, $^{1}J_{C,P} = 23.5$ Hz), 22.1 (s, P*C*H), 22.0 (pseudo-t, $CH(CH_3)_2$, $^{2}J_{C,P} = 6.9$ Hz), 21.8 (s, $CH(CH_3)_2$), 21.7 (pseudo-t, $CH(CH_3)_2$, $^{2}J_{C,P} = 1.6$ Hz), 21.0 (pseudo-t, $CH(CH_3)_2$, $^{2}J_{C,P} = 2.0$ Hz), B-*C* not observed. MS (EI 70 eV) *m*/*z*: 406 $(M)^+$, 349 $(M - t\text{Bu})^+$, 315 $(M - t\text{Bu} - Cl)^+$.

Synthesis of 1,3-Diborata-2,4-diphosphoniocyclobutane (4). A 115 μL (0.231 mmol) portion of HCl (2 M in Et_2O) was added at −78 °C to a solution of compound **3** (90 mg, 0.231 mmol) in pentane (2 mL). After the solution was stirred for 10 min at −78 °C, the discoloration was complete. ^{1}H NMR spectroscopy of the crude mixture allowed to observe the formation of a major compound (>92%). The solution was concentrated and kept in a freezer to yield colorless crystals suitable for X-ray analysis. Yield 37 mg (37%); mp 141 °C. ^{31}P NMR (201 MHz, $CDCl_3$): δ_{ppm} 6.3 (broad). ^{11}B-NMR (160 MHz, $CDCl_3$): δ_{ppm} 6.7 (s, *B*Cl), −18.4 (s, *B*H). ^{1}H NMR (500 MHz, $CDCl_3$): δ_{ppm} 7.44 (d, $^{3}J_{H,H} = 7.8$ Hz, 2H, Ph-*o*-CH), 7.19 (pseudo-t, $^{3}J_{H,H} = 7.8$ Hz, 2H, Ph-*m*-CH), 7.13 (t, $^{3}J_{H,H} = 7.1$ Hz, 1H, Ph-*p*-CH), 3.39 (broad, 1H, B*H*), 2.71 (m, 4H, PC*H*), 1.49 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.47 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.40 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.24 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.14 (s, 9H, $C(CH_3)_3$). $^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$): δ_{ppm} 135.6 (s, Ph-*o*-CH), 127.0 (s, Ph-*m*-CH), 125.0 (s, Ph-*p*-CH), 30.7 (s, $C(CH_3)_3$), 27.2 (pseudo-t, P*C*H, $^{1}J_{C,P} = 22.7$ Hz), 23.3 (pseudo-t, P*C*H, $^{1}J_{C,P} = 7.2$ Hz), 22.2 (s, $CH(CH_3)_2$), 21.7 (s, $CH(CH_3)_2$), 21.4 (s, $CH(CH_3)_2$), 20.5 (s, $CH(CH_3)_2$), B*C* not observed. MS (ESI^+) *m*/*z*: 449 $(M + Na)^+$, 391 $(M - t\text{Bu})^+$, 315 $(M - t\text{Bu} - H + Na)^+$.

Synthesis of 1,3-Diborata-2,4-diphosphoniocyclobutane (5). A 20 μL (0.226 mmol) portion of HOTf was added at −78 °C to a solution of compound **3** (90 mg, 0.231 mmol) in pentane (2 mL). After the solution was stirred for 2 h at −78 °C, the discoloration was complete. ^{1}H NMR spectroscopy of the crude mixture allowed observation of the formation of a major compound (>90%). The solution was filtered and then concentrated and kept in a freezer to yield colorless crystals suitable for X-ray analysis. Yield 25 mg (20%); mp 155 °C. ^{31}P NMR (121 MHz, C_6D_6): δ_{ppm} 3.9 (broad). ^{11}B-NMR (96 MHz, C_6D_6): δ_{ppm} 4.9 (s, *B*OTf), −18.3 (s, *B*H). ^{19}F-NMR (300 MHz, C_6D_6): −78.1. ^{1}H NMR (300 MHz, C_6D_6): δ_{ppm} 7.49 (d, $^{3}J_{H,H} = 7.5$ Hz, 2H, Ph-*o*-CH), 7.25 (pseudo-t, $^{3}J_{H,H} = 7.5$ Hz, 2H, Ph-*m*-CH), 7.18 (t, 1H, Ph-*p*-CH), 3.85 (broad, 1H, B*H*), 2.76 (m, 4H, C*H*$(CH_3)_2$), 2.37 (m, 4H, PC*H*), 1.43 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 7.5$ Hz, 6H, $CH(CH_3)_2$), 1.33 (s, 9H, $C(CH_3)_3$), 1.26 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 7.5$ Hz, 6H, $CH(CH_3)_2$), 1.24 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 7.5$ Hz, 6H, $CH(CH_3)_2$), 1.01 (pseudo-q, $^{3}J_{P,H} = {}^{3}J_{H,H} = 7.5$ Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$-NMR (75.5 MHz, C_6D_6): δ_{ppm} 136.2 (s, Ph-*o*-CH), 127.5 (s, Ph-*m*-CH), 125.7 (s, Ph-*p*-CH), 119.2 (q, $^{1}J_{C,F} = 317.5$ Hz, *C*F_3), 31.6 (s, $C(CH_3)_3$), 28.8 (pseudo-t, P*C*H, $^{1}J_{C,P} = 23.2$ Hz), 23.7 (pseudo-t, P*C*H, $^{1}J_{C,P} = 7.0$ Hz), 22.7 (s, $CH(CH_3)_2$), 22.3 (s, $CH(CH_3)_2$), 21.7 (s, $CH(CH_3)_2$), 21.5 (s, $CH(CH_3)_2$), B*C* not observed. MS (EI 70 eV) *m*/*z*: 540 $(M)^+$, 470 $(M - H - CF_3)^+$, 391 $(M - OTf)^+$.

Synthesis of 1,3-Diborata-2,4-diphosphoniocyclobutane (6). A 42 μL portion of (0.475 mmol) of HOTf was added at −78 °C to a solution of compound **1** (175 mg, 0.473 mmol) in toluene (4 mL). After the solution was stirred for 1 h at −78 °C, the discoloration was complete. ^{1}H NMR spectroscopy of the crude mixture allowed to observe the formation of a major compound (>90%). The toluene was evaporated, pentane was added (4 mL), and the solution was filtered. The solution was concentrated and kept in a freezer to yield colorless crystals suitable for X-ray analysis. Yield 112 mg (45%); mp 105 °C. ^{31}P NMR (201 MHz, C_6D_6): δ_{ppm} 3.2 (broad). ^{11}B-NMR (160 MHz, C_6D_6): δ_{ppm} 6.2 (s, *B*OTf), −17.9 (s, *B*H). ^{19}F-NMR (200 MHz, C_6D_6): −76.7. ^{1}H NMR

(29) The key alkyl alkene intermediates $[Cp_2Zr(Me)(alkene)]^+$ in olefin polymerization have been recently characterized spectroscopically. The ^{13}C NMR data combined with DFT calculations support a strongly dissymmetric coordination of the alkene with major contribution of the η^1 carbocationic structure:(a) Vatamanu, M.; Stojcevic, G.; Baird, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 454–456. (b) Sauriol, F.; Wong, E.; Leung, A. M. H.; Donaghue, I. E.; Baird, M. C.; Wondimagegn, Ziegler, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3342–3345. For related $[Cp_2Zr(Ot\text{-}Bu)(alkene)]^+$ complexes, see: (c) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222–3223. (d) Stoebenau, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 8162–8175.

Table 2. Crystallographic Data for Compounds **2**, **4**, **5**, and **6**

	2	**4**	**5**	**6**
empirical formula	$C_{20}H_{47}B_2ClP_2$	$C_{44}H_{86}B_4Cl_2P_4$	$C_{23}H_{43}B_2F_3O_3P_2S.1/2$pentane	$C_{21}H_{47}B_2F_3O_3P_2S$
formula weight	406.59	853.15	576.27	520.21
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	Cc
a, Å	9.7254(9)	13.177(1)	32.322(1)	11.5692(7)
b, Å	11.386(1)	14.246(2)	11.0928(4)	16.160(1)
c, Å	22.736(2)	14.621(1)	19.4956(6)	15.866(1)
α, deg	92.369(2)	67.428(1)	90	90
β, deg	96.916(2)	88.668(1)	114.759(2)	108.836(1)
γ, deg	97.929(2)	87.489(1)	90	90
V, Å^3	2471.1(4)	2532.0(3)	6347.5(4)	2807.4(3)
Z	4	2	8	4
density$_{calcd}$, Mg/m^3	1.093	1.119	1.206	1.231
abs coeff, mm^{-1}	0.287	0.283	0.245	0.269
reflns collected	11077	17763	27869	8203
independent reflns	6983	8463	4657	4081
$R1$ ($I > 2\sigma(I)$)	0.0589	0.0370	0.0483	0.0313
wR2	0.1283	0.0864	0.1060	0.0777
(Δ/r)max (e Å^{-3})	0.806 and −0.322	0.426 and −0.238	0.370 and −0.272	0.344 and −0.200

(500 MHz, C_6D_6): δ_{ppm} 2.80 (m, 2H, PC*H*), 2.57 (broad, 1H, B*H*), 2.25 (m, 3H, PC*H* + C*H*(CH$_3$)$_2$), 1.38 (m, 8H, CH(*CH*$_3$)$_2$+ C*H*$_2$), 1.32 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.26 (pseudo-q,$^3J_{P,H}$ = $^3J_{H,H}$ = 7.1 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (pseudo-q,$^3J_{P,H}$ = $^3J_{H,H}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (s, 9H, C(C*H*$_3$)$_3$), 1.21 (pseudo-q, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-NMR (125 MHz, C_6D_6): δ_{ppm} 119.2 (q, $^1J_{C,F}$ = 317.5 Hz, *C*F$_3$), 34.8 (s, C(*C*H$_3$)$_3$), 30.0 (s, *C*H$_{2(i\text{-Bu})}$), 26.6 (pseudo-t, P*C*H, $^1J_{C,P}$ = 7.0 Hz), 25.7 (s, CH(*C*H$_3$)$_{2(i\text{-Bu})}$), 23.9 (pseudo-t, P*C*H, $^1J_{C,P}$ = 24.0 Hz), 20.9 (m, P*C*H + CH(*C*H$_3$)$_{2(i\text{-Pr})}$), 20.0 (s, 2 CH(*C*H$_3$)$_{2(i\text{-Pr})}$), 19.7 (s, CH(*C*H$_3$)$_{2(i\text{-Pr})}$), B-*C* not observed. MS (EI 70 eV) *m*/*z*: 520 (M)$^+$, 463 (M − *t*Bu)$^+$.

Crystal Structure Determination of Compounds 2, 4, 5, and 6 (Table 2). Data for all structures were collected at 193(2) K using a oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.7103 Å). Semiempirical absorption corrections were employed for compounds **2**, **4**, and **6**.[30] The structures were solved by direct methods (SHELXS-97)[31] and refined using the least-squares method on F^2.[32]

Computational Details. Phosphorus and chlorine were treated with a Stuttgart−Dresden pseudopotential in combination with their adapted basis set.[33] In all cases, the basis set has been augmented by a set of polarization function (d for P and Cl).[34,35] Carbon, boron, and hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set.[36] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[37,38] Geometry optimizations were carried out without any symmetry restrictions, the nature of the extrema (minimum) was verified with analytical frequency calculations. The intrinsic reaction coordinate has been followed using the IRC technique for all located transition states. All these computations have been performed with the Gaussian 03[39] suite of programs.

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Supporting Information Available: Complete ref 39 citation; Cartesian coordinates for the optimized structures, ^{1}H NMR spectra and crystallographic data for compounds **2**,**4**,**5** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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