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Terpene Dispersion Energy Donor Ligands in Borane Complexes

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Structural characterization of the complex [B(β-pinane)$_3$] (1) reveals non-covalent H···H contacts that are consistent with the generation of London dispersion energies involving the β-pinane ligand frameworks. The homolytic fragmentations of 1, and camphane and sabinane analogues ([B(camphane)$_3$] (2) and [B(sabinane)$_3$] (3)) were studied computationally. Isodesmic exchange results showed that London dispersion interactions are highly dependent on the terpene's stereochemistry, with the β-pinane framework providing the greatest dispersion free energy (ΔG = -7.9 kcal mol^{-1}) with Grimme's dispersion correction (D3BJ) employed. PMe$_3$ was used to coordinate to [B(β-pinane)$_3$], giving the complex [Me$_3$P–B(β-pinane)$_3$], which displayed a dynamic coordination equilibrium in solution. The association process was found to be slightly endergonic at 302 K (ΔG = +0.29 kcal mol^{-1}).

Alkyl borane complexes featuring terpenoid substituents (naturally occurring compounds derived from the 5-carbon isoprene),[1,2] have been used since the early 1960s as asymmetric catalysts for stereoselective reductions of various pro-chiral substrates. The pioneering work of H. C. Brown[3–8] and coworkers on the formation of organoboranes via anti-Markovnikov hydroboration gave ready access to complexes of this type, including industrially relevant terpenes such as α- and β-pinene (Fig. 1), as well as many other useful derivatives. Since then, the hydrogenated β-pinane substrate has become ubiquitous in organic chemistry, as well as its borane complexes (of the formula [BH$_2$R] and [BR$_3$], R = β-pinane) for example, in Suzuki-Miyaura cross-coupling[9] and radical chain reactions.[10] Computational studies on terpene molecules have revealed

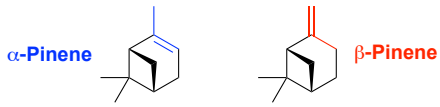

Figure 1. Structures of α–Pinene and β–Pinene.

that the conformational changes they display are highly dependent on inherent intramolecular London dispersion (LD) interactions between the C–H moieties of their cyclic structures.[11] Furthermore, density functional theory (DFT) calculations performed with use of Grimme's dispersion correction,[12,13] have indicated that in substituted cyclohexanes, the greatest stabilization is generated when the cyclic systems are in an axial conformation, due to the resultant eclipsed nature of these groups.[11,14] LD effects in complexes containing these cyclic substituents, for example in H. C. Brown's terpane-boranes, are therefore likely significant when considering their structure and stereoselective properties. We have recently investigated dispersion enhanced donor (DED)[15] ligands and consider terpenes, particularly those featuring multicyclic frameworks such as β-pinene, to have potential in producing DED effects. Theoretical studies further suggested that terpenes acting as DED ligands would provide valuable insight into LD effects in molecular complexes, and how structural conformations affect subsequent reactivity. The introduction of DED ligands has allowed the characterization of otherwise non-isolable species,[16–21] and DED ligands have also been shown to be important for understanding previously established reactivities, for example in the formation of alkoxides[22] or enzyme-relevant thiourea catalysts.[23] While larger ligands provide kinetic stabilization, many studies have demonstrated the importance of the underpinning LD interactions within these ligand frameworks which also give rise to stabilizing effects.[24,25]

Here, we report the synthesis, characterization, and computational analysis of a range of trialkylboranes using the isomeric multicyclic terpenes, β-pinene (**1**), camphene (**2**), and sabinene (**3**) as well as a Lewis pair complex (**4**) (Scheme 1). The homoleptic tris-alkylboranes (**1**–**3**) were synthesized by the

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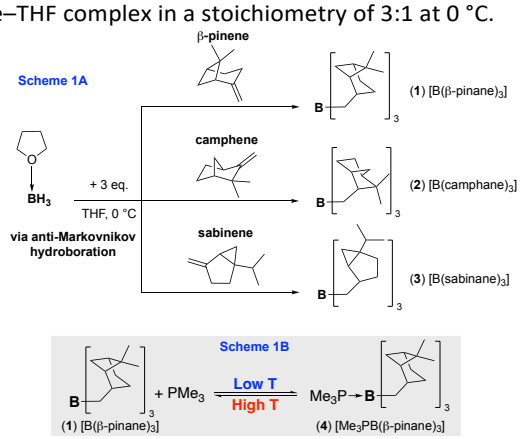
anti-Markovnikov hydroboration of the terpene, using a borane–THF complex in a stoichiometry of 3:1 at 0 °C.



Scheme 1. (A) Synthetic route towards the isomeric complexes **1**–**3** and **4** (B).

Despite the original isolation of complex **1**, [B(β-pinane)$_3$] in 1964,[3] it has not been crystallographically characterized. The single-crystal X-ray crystallographic analysis of this complex, which very clearly displays the DED effects of the β-pinane substituents when bonded to the boron atom is shown in Fig. 2. X-ray analysis of **1** showed the expected trigonal-planar structure and boron atom with a sp^2-valence electron configuration, but also a confacial arrangement of the β-pinane ligands in an axial fashion, suggesting a highly stable conformation.

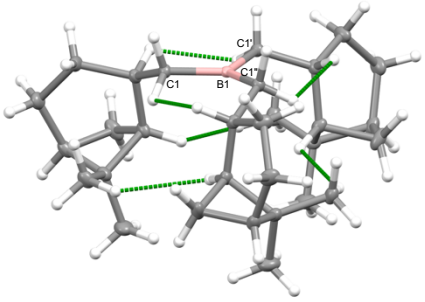


Figure 2. Molecular structure of compound **1**, [B(β-pinane)$_3$]. Thermal ellipsoids shown at 50% probability. Inter-ligand H···H close contacts are shown in green. Selected bond lengths and angles in **1** include B1–C1 = 1.5811(11) Å, C1'–B1–C1 = 119.735(17)°.

The unusual structure of complex **1** deviates from other tris-alkylborane species, where one might expect at least one ligand to lie on the opposite side of the B(C)$_3$ plane, such that steric repulsion would be minimized. The B(1)–C(1) bond length is 1.5811(11) Å (similar to that in [BCy$_3$][26] and [B(2,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$][27] with B–C bond lengths of 1.589(5) Å and 1.583(3) Å respectively) and the C1–B1–C1' angle is 119.735(17)° (very close to the trigonal planar value of 120.00° in [BCy$_3$] and 119.11° in [B(2,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$]). The coordinated axial arrangement of the β-pinane substituent moieties can be rationalized by the stability induced by attractive LD interactions between the H···H and C···H intramolecular close contacts, which are less than the sum of van der Waals (vdW) radii (2.4 Å) observed between the β-pinane ligands. The ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra of complex **1** agreed with previous reports.[9] The isomeric boranes [B(camphane)$_3$] (**2**) and [B(sabinane)$_3$] (**3**) could only be obtained as a gel and oil respectively, with spectral analysis indicating mixtures of products. The ^{11}B NMR spectra obtained for **2** and **3** did show signals at δ = 87.8 and 87.5 ppm respectively, suggesting partial conversion to the tri-substituted boranes. As complexes **2** and **3** proved difficult to isolate, DFT structure optimizations were carried out to model these complexes, as well as complex **1** for comparison (Fig. 3) at the PBE1PBE-D3BJ/Def2-TZVP level.

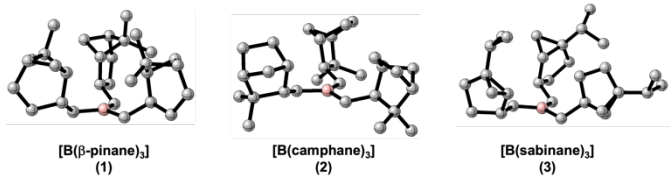


Figure 3. DFT-optimized structures of complexes **1**–**3** at the PBE1PBE-D3BJ/Def2-TZVP level. Boron shown in pink, carbon in grey and hydrogens are not shown.

We began the DFT study by screening different orientations of the ligands in compounds **2** and **3** to determine the most stable configuration, as no experimentally determined molecular structures were available. Few stable minima structures were located, but those presented are clearly the most favored by energy considerations (ESI). In addition, the DFT-optimized structure for [B(β-pinane)$_3$] (**1**) corresponds well with the X-ray derived molecular structure which also displays a clustering of the β-pinane ligands on one side. Less intramolecular attraction between the camphane groups in **2** was observed, and the least attraction between the sabinane groups in **3**, with the isopropyl tails of this ligand being orientated away from each other. For a further comparison of the energy contributions from LD interactions, we performed isodesmic exchange calculations[28] on each of the complexes. This isodesmic exchange describes the putative conversion of three dihydroalkylboranes to the tris-alkylborane and two BH$_3$ molecules.[29,30] Each side of this theoretical reaction contains an equivalent number of each type of B–R bond, and thus the effect of dispersion interactions between the ligands can be assessed. The results of the theoretical isodesmic exchange reaction are shown in Fig. 4. In the absence of Grimme's dispersion correction (D3BJ),[31,32] the calculated free energies were found to be similar in all three complexes (ΔG = +9.3 kcal mol^{-1} for **1**, +10.3 kcal mol^{-1} for **2** and +10.6 kcal mol^{-1}). The calculated free energies when Grimme's dispersion correction is applied showed a more thermodynamically favorable formation of [B(β-pinane)$_3$] (ΔG = +1.4 kcal mol^{-1}) versus the [B(camphane)$_3$] and [B(sabinane)$_3$] isomers (ΔG = +3.7 and +5.2 kcal mol^{-1} respectively). The calculated free energy gain (for the conversion of [H$_2$BR] to [BR$_3$] and [BH$_3$]) with dispersion correction afforded ΔG = -7.9 kcal mol^{-1} for [B(β-pinane)$_3$]. This reflects the conversion of zero β-pinane···β-pinane interactions in the putative [BH$_2$(β-pinane)] to 6 new interactions between each of the β-pinane ligands in the formed [B(β-pinane)$_3$]. The dispersion free energy (ΔG) derived from the same approach for the isomers [B(camphane)$_3$] and [B(sabinane)$_3$] were calculated to be ΔG = -6.6 and -5.4 kcal mol^{-1} respectively. Table S4 (ESI) lists the corresponding reaction energies (ΔE) and ΔG at the

PBE1PBE/Def2-TZVP level of theory, with and without Grimme's dispersion correction applied (illustrated in Figure 4).

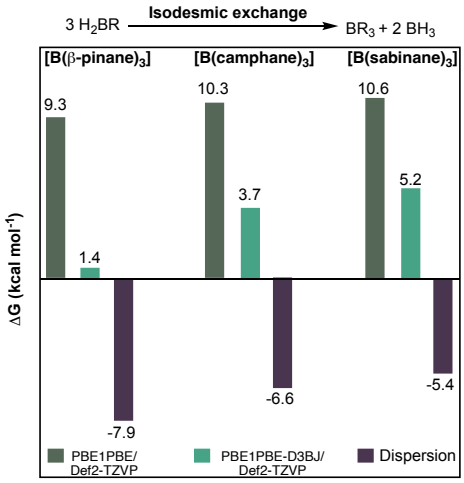


Figure 4. Calculation results from an isodesmic exchange reaction regarding $[B(R)_3]$, where R = Sabinane, Camphane and Pinane.

To chemically investigate the strength of the LD interactions between the β-pinane ligands in complex **1**, we employed the Lewis base PMe_3 to form complex **4**, $[Me_3P–B(\beta\text{-pinane})_3]$ (Scheme 1B), comparable to previously reported frustrated Lewis pairs (FLPs),[33–35] though few PMe_3 trialkylborane complexes are known. The interligand H···H close contacts (less than the sum of vdW radii of 2.4 Å) between the calculated hydrogen positions decorating the β-pinane frameworks in **1** are shown in Fig. 2. Crystals suitable for X-ray studies of $[Me_3P–B(\beta\text{-pinane})_3]$ were isolated from a concentrated pentane solution at -33 °C. Structural comparisons of **1** and **4** are shown in Fig. 5. The molecular structure of $[Me_3P–B(\beta\text{-pinane})_3]$ displays the separation of the β-pinane ligands on the geometry change of the boron to tetrahedral. In addition, the observed B1–P1 bond length of 2.017(12) Å in $[Me_3P–B(\beta\text{-pinane})_3]$ is significantly shorter (< 3σ) than that in $[Ph_3P–B(C_6F_5)_3]$ with a B–P bond length of 2.181(6) Å, likely due to steric considerations.[36] The comparison shown in Fig. 5 provides an illustration of the dynamic behavior of the β-pinane ligands crowding due to LD interactions, which are subsequently forced apart (diminishing the highly distance-dependent LD effects) when **1** is complexed with PMe_3. The ^{1}H NMR spectrum of **4** displayed two signals assignable to the PMe_3, suggesting dynamic behavior in solution. ^{31}P NMR spectroscopy afforded a slightly broadened signal at δ = -39.8 ppm at room temperature. Many studies on solution-state dynamics[37–40] for ligand complexation have been reported.

Variable temperature (VT) ^{31}P NMR experiments (Fig. S8, ESI) showed that at higher temperatures, a fast equilibrium occurs between the formation of complex **4** and the starting materials PMe_3/$[B(\beta\text{-pinane})_3]$, where the phosphorus remains shielded and donation to the boron is limited. At 358.0 K the observed ^{31}P chemical shift (δ = -51.9 ppm) more closely resembles that of free PMe_3 (δ = -62.3 ppm). Upon cooling, electron donation to the boron increases and the phosphorus becomes more de-shielded which is consistent with the

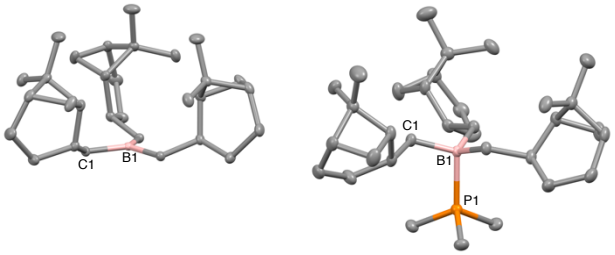


Figure 5. Molecular structure of complex **4** (thermal ellipsoids at 50% probability), $[Me_3P–B(\beta\text{-pinane})_3]$ (right) compared with complex **1** (left). Selected bond lengths (Å) and angles (°) in **4** include B1–P1 = 2.017(12), B1–C1 = 1.640(7), P1–B1–C1 = 107.1(5). Hydrogens are not shown for clarity.

chemical shift moving downfield. At 273.0 K, the signal begins to broaden significantly and at 250.0 K is resolved into two separate signals, a process that is approximately complete at 233.0 K (δ = -10.3 and -62.3 ppm). These shifts become highly resolved at 209.0 K, where the signal corresponding to $[Me_3P–B(\beta\text{-pinane})_3]$ is found at δ = -9.5 ppm, and free PMe_3 at δ = -62.3 ppm. The corresponding ^{11}B signal at 209.0 K was found at δ = -14.5 ppm with no $^1J_{BP}$ coupling observed. The ^{31}P NMR shift of δ = -9.5 ppm for $[Me_3P–B(\beta\text{-pinane})_3]$ is similar to other borane–phosphine complexes, such as those found for $[Ph_3P–B(C_6F_5)_3]$[36] and $[Me_3P–B(Ph)Cp_2ZrCl_2]$[41] which have a ^{31}P shift of δ = -5.2 and -14.8 ppm respectively. Van't Hoff analysis (ESI) was used to determine the thermochemical parameters of the association reaction. The enthalpy of the association was found to be slightly exothermic, ΔH = -1.55 kcal mol^{-1} with the entropy contribution minimal (ΔS = -0.006 kcal mol^{-1} K^{-1}). Using these parameters, the free energy of association at each temperature was calculated (results are displayed in Fig. S14, ESI). These indicate that at lower temperatures, the formation (association) of $[Me_3P–B(\beta\text{-pinane})_3]$ is thermodynamically favored in the range of 209 K and 250 K between ΔG = -0.27 and -0.02 kcal mol^{-1} respectively. At temperatures above 250 K, the -$T\Delta S$ component of the free energy becomes more positive, resulting in the dissociation of $[Me_3P–B(\beta\text{-pinane})_3]$ (ΔG = +0.03 – +0.65 kcal mol^{-1} between 258 K and 358 K, thermodynamically disfavored). These findings are comparable to the endergonic free energy of association of $[^tBu_3P–B(C_6F_5)_3]$ (ΔG = +0.40 kcal mol^{-1} at 298 K)[42] while the association of $[Me_3P–B(\beta\text{-pinane})_3]$ at 302 K has a ΔG = +0.29 kcal mol^{-1}. This association equilibrium found for **4** is akin to that displayed by FLPs.[33–35] These determined thermochemical parameters are likely due to a combination of sterics and electronics. At higher temperatures, the β-pinane ligand fluxionality (evident from ^{1}H VT-NMR, Fig. S8, ESI) inhibits PMe_3 coordination, while at lower temperatures the β-pinane ligands cluster on one side (Fig. 2), and so the PMe_3 coordination must overcome their LD attraction. Though the association is endergonic at 298 K, at lower temperatures the isolation of **4** is likely aided by LD interactions generated between the β-pinane substituent hydrogens and the methyl groups of the PMe_3 (Fig. S16, ESI). Computational analysis of the association reaction for complex **4** found the process to be exergonic in the gas phase (ΔG= -0.13 kcal mol^{-1} at 298 K). The enthalpy and entropy of association were found to be more exothermic (ΔH = -11.8 kcal mol^{-1}) and entropically disfavored

(ΔS = -0.039 kcal mol^{-1} K^{-1}) at 298 K. In the absence of dispersion correction, the association was found to be endergonic (ΔG = +7.86 kcal mol^{-1}) at 298 K. The experimental and computational discrepancies in the thermodynamic parameters obtained are likely due to the solvent-free model applied.

In summary, in the isomers β-pinane, sabinane, and camphane, the stereochemical arrangement of the β-pinane derivative has the highest LD effect in the series of homoleptic tris-alkylborane congeners. This allowed crystallographic analysis of [B(β-pinane)$_3$] (**1**) for the first time. The structure clearly displays a counterintuitive clustering of the β-pinane substituents on one side of the B(C)$_3$ plane. Isodesmic exchange calculations suggest that this is due to LD interactions between the β-pinane substituents, with a dispersion energy of ΔG = -7.9 kcal mol^{-1} at 298 K. This was found to be more thermodynamically favorable than the isomers [B(camphane)$_3$] (**2**) and [B(sabinane)$_3$] (**3**) (ΔG = -6.6 and -5.4 kcal mol^{-1} respectively). VT-NMR experiments on the Lewis pair complex [Me$_3$P–B(β-pinane)$_3$] (**4**) showed dynamic behavior in solution. Van't Hoff analysis revealed that at 302 K, the free energy of association of compound **4** was +0.29 kcal mol^{-1} (slightly endergonic). These findings highlight the rapidly burgeoning interest in LD effects on both inorganic and organic synthesis.

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