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Highly Fluorinated Aryl-Substituted Tris(indazolyl)borate Thallium Complexes: Diverse Regiochemistry at the B−N Bond

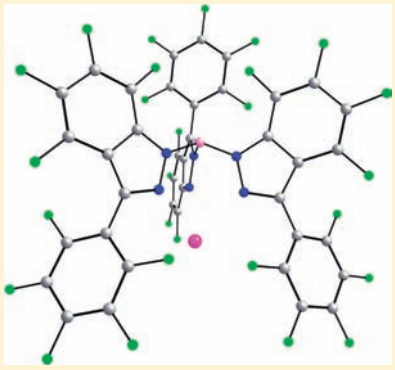
Wilfried-Solo Ojo,[†,‡] Kane Jacob,[†,‡] Emmanuelle Despagnet-Ayoub,[†,‡] Bianca K. Muñoz,[†,‡] Sergio Gonell,[†,‡] Laure Vendier,[†,‡] Viet-Hoang Nguyen,[†,‡] and Michel Etienne*[,†,‡]

[†]CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, F-31077 Toulouse, France

[‡]Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse, France

Supporting Information

ABSTRACT: The synthesis and characterization (mainly by ^{19}F NMR and X-ray diffraction) of highly fluorinated aryl-4,5,6,7-tetrafluoroindazoles and their corresponding thallium hydrotris(indazolyl)borate complexes are reported [aryl = phenyl, pentafluorophenyl, 3,5-dimethylphenyl, 3,5-bis(trifluoromethyl)phenyl]. Thanks to N−H···N hydrogen bonds, the indazoles crystallize as dimers that pack differently depending on the nature of the aryl group. The thallium hydrotris(indazolyl)borate complexes Tl[Fn-Tp^{4Bo,3aryl}] resulting from the reaction of aryl-4,5,6,7-tetrafluoroindazoles [aryl = phenyl, 3,5-dimethylphenyl, 3,5-bis(trifluoromethyl)phenyl] with thallium borohydride adopt overall C_{3v} symmetry with the indazolyl groups bound to boron via their N-1 nitrogen in a conventional manner. When the perfluorinated pentaphenyl-4,5,6,7-tetrafluoroindazole is reacted with thallium borohydride, a single regioisomer of C_s symmetry having one indazolyl ring bound to boron via its N-2 nitrogen, TlHB(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-1-yl)$_2$(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-2-yl) Tl[F27-Tp$^{(4Bo,3C6F5)*}$], is obtained for the first time. Surprisingly, the perfluorinated dihydrobis(indazolyl)borate complex Tl[F_{18}-Bp^{3Bo,3C6F5}], an intermediate on the way to the hydrotris(indazolyl)-borate complex, has C_s symmetry with two indazolyl rings bound to boron via N-2. The distortion of the coordination sphere around Tl and the arrangement of the complexes in the crystal are discussed.



INTRODUCTION

As a consequence of its strong electronegativity and hardness, fluorine imparts unique properties to organic or inorganic compounds that extend to intermolecular interactions and supramolecular chemistry.[1] Fluorinated ligands exhibit high electron-withdrawing properties and good oxidative stability which yields stable yet strongly electrophilic metal centers. Tris(pyrazolyl)borates have been extensively used as ligands in inorganic and organometallic chemistry because of their pocket-type configuration affording a good protection around the metal center and an easy tuning of their electronic and steric properties.[2] Up to now, only few examples of fluorinated scorpionate ligands were synthesized because of limitation of the synthetic methologies.[3] On the basis of indazolyl units, we recently reported a perfluorinated hydrotris(3-trifluoromethylindazol-1-yl)borate and its use in alkane activation.[4] Interested in fine-tuning the electronic and steric properties of the fluorinated tris(indazolyl)borate ligands, we investigated the synthesis and structures of aryl-substituted hydrotris(indazolyl)borates [aryl = phenyl, pentafluorophenyl, 3,5-dimethylphenyl and 3,5-bis(trifluoromethyl)phenyl] and their thallium complexes.

Unsubstituted hydrotris(indazolyl)borates adopt a so-called "abnormal" regiochemistry where boron is apparently bound to the more sterically hindered, yet electronically richer, nitrogen as in **a** (R = H, a Tp^{4Bo} following Trofimenko's nomenclature) instead of **b** (Tp^{3Bo}) (Chart 1).[5] When substitution occurs at position 3 (e.g., R = Me, as in Tp^{4Bo,3Me}), the same pattern **a** is then referred to as "normal" since the largest substituent is placed away from boron,[6] in contrast to hydrotris(pyrazolyl)-borates where the bulky substituent virtually always ends up at position 3.[2,7]

For homoscorpionates based on indazoles, all thallium compounds are of C_{3v}, type **a**, symmetry except for those containing a 7-alkyl substituent and those obtained from 3-methylnaphtopyrazole for which a 2:3 mixture of hydrotris(3-methyl-2*H*-benz[*g*]indazol-2-yl) (type **b**) and hydrobis(3-methyl-2*H*-benz[*g*]indazol-2-yl)(3-methyl-2*H*-benz[*g*]indazol-1-yl)borate (C_s, type **c**, Scheme 1) was observed.[6] To the best of our knowledge, no C_s symmetric complex of type **d** has ever been described. Herein we report the synthesis and the structural characterization of a family of aryl-4,5,6,7-tetrafluoroindazoles and their related fluorinated hydrotris(arylindazolyl)borates. The expected C_{3v} structure Tl[F12-Tp^{4Bo,3Ph}] (**Tl-1**),[8] Tl[F12-Tp$^{4Bo,3(3,5\text{-}Me2C6H3)}$] (**Tl-3**), and Tl[F30-Tp$^{4Bo,3(3,5\text{-}(CF3)2C6H3)}$] (**Tl-4**) is obtained from 3-phenyl-4,5,6,7-tetrafluoro-1*H*-indazole, 3-(3,5-dimethylphenyl)- and 3-(3,5-bis(trifluoromethyl)phenyl)-indazoles, respectively. In complete contrast, when the highly electron poor 3-

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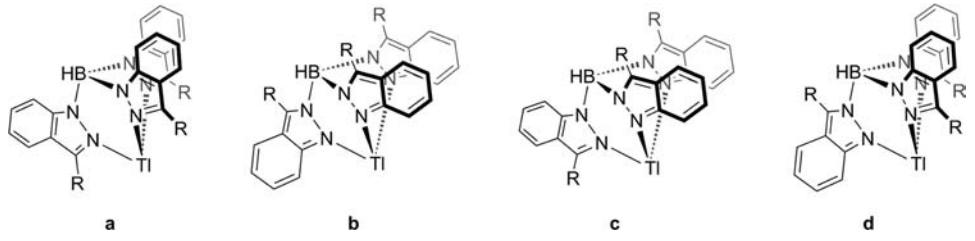
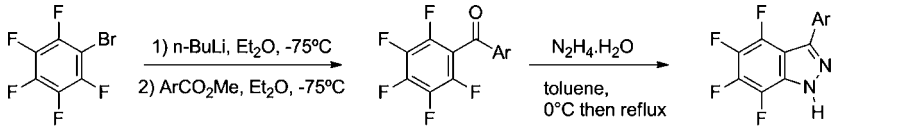
Chart 1. Regiochemistry of Thallium Hydrotris(indazolyl)borates



Scheme 1. Synthesis of Aryl-4,5,6,7-tetrafluoroindazoles 1, 2, 3, and 4



1: Ar = Ph, *95%*
2: Ar = C_6F_5, *90%*
3: Ar = 3,5-$Me_2C_6H_3$, *37%*
4: Ar = 3,5-$(CF_3)_2C_6H_3$, *83%*

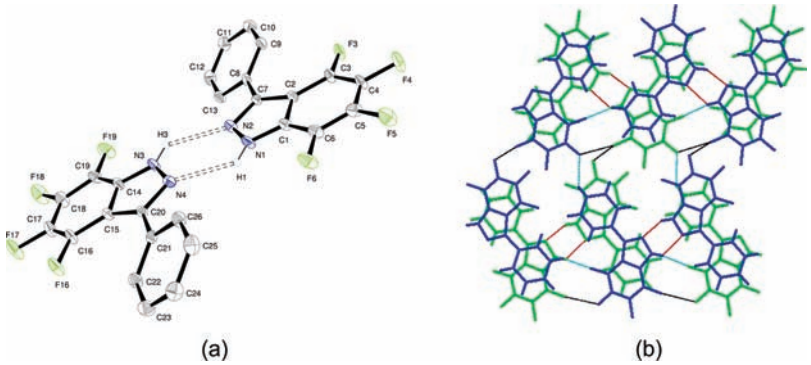


Figure 1. (a) Molecular view of **1**; (b) Packing diagram of **1** along the *a* axis; for clarity the molecules from the same layer are drawn with the same color; intermolecular interactions are marked as dotted lines (red: NH···N hydrogen bonds, black: F···F, pale blue: NH···F).

pentafluorophenyl-4,5,6,7-tetrafluoro-1*H*-indazole is reacted with $TlBH_4$, a C_s structure is *exclusively* formed in TlHB(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-1-yl)$_2$(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-2-yl), Tl[F27-$Tp^{(4Bo,3C6F5)*}$] (**Tl-2**), the first **d**-type complex ever reported (Chart 1). We have also discovered that the bis(indazolyl)-borate synthesized from 3-phenyl-4,5,6,7-tetrafluoro-1*H*-indazole, an intermediate in the synthesis of **Tl-2**, is indeed of C_s symmetry but exhibits an "abnormal" regiochemistry with TlH_2B(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-2-yl)$_2$ Tl[F18-$Bp^{3Bo,5C6F5}$] (**Tl-5**) being formed, indicating that complex rearrangements do take place in poly(indazolyl)borate thallium chemistry.

RESULT AND DISCUSSION

Synthesis and Characterization of Aryl-4,5,6,7-tetrafluoroindazoles. Indazoles were synthesized following the reported procedure for 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole.[9] Pentafluorobromobenzene was treated by *n*-butyllithium at low temperature followed by addition of the corresponding methyl benzoate to generate the pentafluorobenzophenone. Then the cyclization was realized by adding hydrazine hydrate and heating the reaction mixture in toluene (Scheme 1). Compounds **1** and **2**, previously synthesized via a slightly different route,[10] were obtained from the commercially available 2,3,4,5,6-pentafluorobenzophenone and decafluorobenzophenone, respectively. Overall yields range from 83 to 95% except for the 3-(3,5-bismethylphenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (**3**) (37%) because of a poor cyclization yield. The new indazoles were spectroscopically and crystallographically characterized. The spectroscopic data for **1** and **2** matched those previously reported.[10] In all compounds, the benzo ring is characterized by four ^{19}F NMR signals more shielded in the sequence F-5 < F-7 < F-6 < F-4 with a unique fine structure. The chemical shift of F-4 (as a pseudo triplet) appears more sensitive to substitution at position 3 (C_6H_5, δ −140.0; C_6F_5, δ −154.6; 3,5-$Me_2C_6H_3$, δ −142.7; 3,5-$(CF_3)_2C_6H_3$, δ −140.0).

In the crystal, indazoles **1**, **2**, and **4** show different packings depending on the aryl substituent. Indeed, **1** crystallizes in the space group $Pbc2_1$ (Figure 1). In the asymmetric unit, two similar but not identical molecules of **1** are connected by two NH···N hydrogen bonds (red lines (Figure 1b): N1−N2 = 1.356(7), N3−N4 = 1.345(6), N1···N4 = 2.86, N2···N3 = 2.87 Å). The dimers are packed as stacked arrays of antiparallel pairs along the *a* axis (Figure 1b). This arrangement is likely the consequence of attractive $\pi-\pi$ interactions between electrodeficient fluorinated benzo rings (C_6F_4) and phenyl (C_6H_5) substituents.[1b,11] The molecules are not planar, the phenyl group being twisted with respect to the fluorinated indazole unit (N2−C7−C8−C13 = −24°; N4−C20−C21−C26 = 25°).

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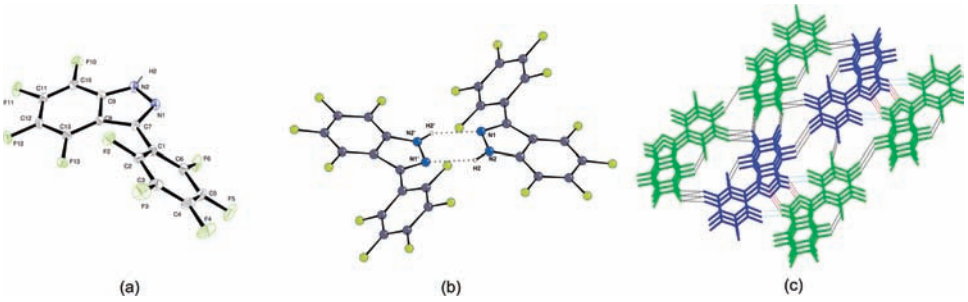


Figure 2. (a) Molecular view of **2**. (b) Dimer formed via N−H···N hydrogen bonds. (c) Packing diagram of **2**; for clarity the chains having the same *c* coordinate are drawn with the same color; intermolecular interactions are marked as dotted lines (red: N−H···H, black: F···F, blue: NH···F).

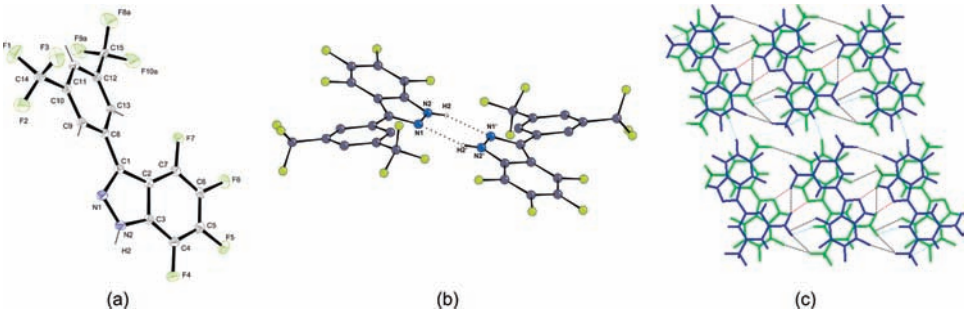
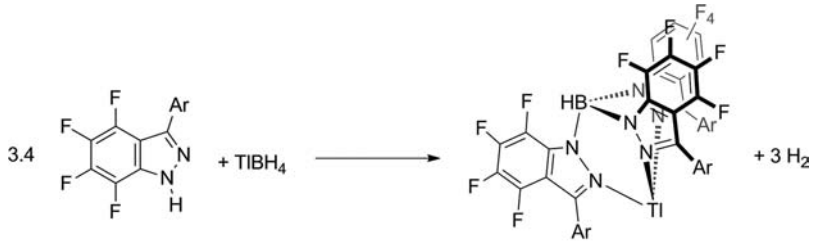


Figure 3. (a) Molecular view of **4**. (b) Dimer formed via N−H···N hydrogen bonds. (c) Packing diagram of **4** along the *b* axis; for clarity the molecules from the same layer are drawn with the same color; intermolecular interactions are marked as dotted lines (red: N−H···H hydrogen bonds, black: F···F, blue: H···F).

Scheme 2. Synthesis of Fluorinated Hydrotris(indazolyl) borates Tl-1, Tl-3, Tl-4



Short contacts, smaller than the van der Waals radii are also apparent (Figure 1b) such as C−F···F−C [black lines: 2.84 Å (126.7, 145.6°) and 2.81 Å (99.6, 139.7°)], N−H···F−C (pale blue lines: N···F 3.10, H···F 2.45 Å; N−H···F 131°, N···F−C 165°) and C−H···F−C (C···F 3.21, H···F 2.45 Å; C−H···F 136, C···F−C 132°). All these interactions participate in the dimers' arrangement in the crystal lattice.[1b,11−13]

Introducing electron-withdrawing fluorines on the phenyl group modifies the crystal packing (Figure 2). Indazole **2** crystallizes in the space group $P\bar{1}$. Two molecules of **2**, related by an inversion center, are connected by N−H···N hydrogen bonds (red lines, Figure 2b; N1−N2 = 1.3542(16) Å, N2···N1′ = 2.85 Å, N2−H2 = 0.851(9) Å; N2−H2···N1′ = 140°). The dimers stack parallel along the *a* axis. The C_6F_5 and the indazolyl moiety are not coplanar with a dihedral angle N2−C7−C1−C6 of −41.5°. Close contacts are noticed as N−H···F−C between a fluorine from a C_6F_5 ring and H2−N2 of a neighboring dimer (pale blue lines; F6···N2 2.98 Å, C6−F6···N2 153°), and C−F···F−C between fluorines of subsequent benzo and C_6F_5 rings (black lines; F13···F2 2.75 Å, C13−F13···F2 135°).[13]

The packing of **4** is similar to that observed for the phenyl tetrafluoroindazole **1** (Figure 3) with an antiparallel motif translated along the *b* axis. This allows a more attractive *π*-stacking between the electron-deficient tetrafluorobenzo ring and the partially fluorinated xylyl moiety. The stacking is overall simpler since the space group is $P2_1/c$ and, as a consequence, the dimers resulting from N−H···N hydrogen bonds are symmetrical. Indazole **4** exhibits a dihedral angle N1−C1−C8−C9 of −22.8° between the 3,5-bis(trifluoromethyl)phenyl and the tetrafluoroindazolyl groups. Short contacts can be highlighted: CF_3···F (black lines (Figure 3b): 2.77−2.93 Å) and H−N···H hydrogen bonds (N1−N2 = 1.340(5) Å, N2···N1′ = 2.90 Å; N2−H2···N1′ = 135°). Moreover the distortion of the xylyl group allows C−H···F interchain interactions [blue lines (Figure 3b): (i) C−H···F_3C: 2.53 Å (121.2, 152.7°); (ii) C−H···F−C_{benzo}: 2.66 Å (145.5, 147.7°)].[13]

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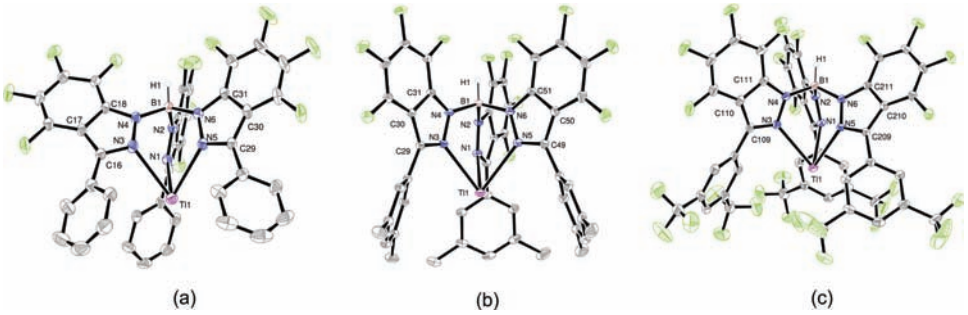
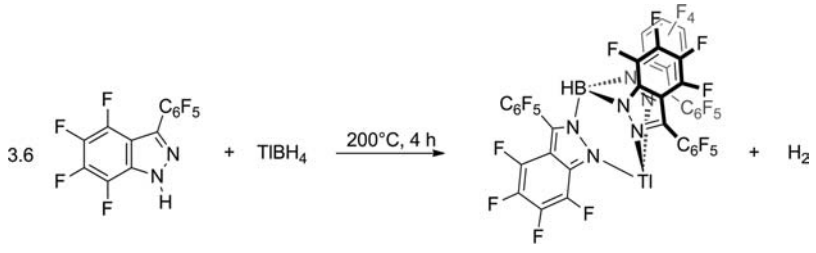


Figure 4. (a), (b), (c) Molecular views of **Tl-1**, **Tl-3**, and **Tl-4**, respectively (For relevant bond length and angles, see Table 1).

Table 1. Selected Intra- and Intermolecular Metrical Parameters for Tl-1, Tl-3, and Tl-4

	compounds		
	Tl-1	**Tl-3**	**Tl-4**
Tl–N (Å)	2.660(4), 2.659(4), 2.615(4)	2.5925(16), 2.6178(16), 2.6450(17)	2.653(3), 2.648(3), 2.645(3)
B–N (Å)	1.554(6), 1.548(6), 1.545(6)	1.555(3), 1.547(3), 1.560(3)	1.542(5), 1.534(5), 1.550(5)
N–Tl–N (deg)	69.57(12) 64.82(12), 75.96(12)	69.44(5), 72.64(5), 69.46(5)	69.98(9), 69.84(9), 75.05(9)
B1–N2–N1–Tl1 (deg)	−24.3	−6.5	22.0
B1–N4–N3–Tl1 (deg)	−28.2	7.9	24.1
B1–N6–N5–Tl1 (deg)	12.4	10.2	38.2
B–N–N–C (deg)	174.1, −165.6, 176.2	161.8, 166.4, 172.9	166.9, 175.9,172.4
π–π: $d_{(plane/plane)}$ (offset) (Å)	N(1)N(2): 3.56 (2.11)	N(1)N(2): 3.46 (2.52)	N(5)N(6): 3.40 (2.31)
	N(3)N(4): 3.37 (1.71)	N(3)N(4): 3.73 (2.20)	
C_{benzo}–F···F–C_{benzo} d (Å) (angles (deg))	2.80 (128.0, 90.8)	2.87	2.78 (171.5, 85.2),
H···F (Å) (angles (deg))	2.63 (131.1, 80.6)	2.59 (165.5, 118.5)	
		2.66 (133.4, 123.6)	
		2.65 (165.0, 109.1)	

Scheme 3. Synthesis of Tl[F27-Tp$^{(4Bo,3C6F5)*}$] (Tl-2)



Interestingly, none of the aryl-substituted fluorinated indazoles **1**, **2**, and **4** pack in a helix fashion like the 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole.[9,14] It is likely that in addition to different steric demands aromatic π–π interactions, whether between fluorinated rings or between fluorinated and hydrogenated rings, overcome those between saturated CH or CF and tetrafluorinated indazolyl rings that lead to crystallizations as catemers.[15]

Synthesis and Characterization of Complexes Tl-1, Tl-3, and Tl-4. Upon reaction with KBH_4, 3-methyl-1*H*-indazole[6a] or its perfluorinated 3-trifluoromethyl-1*H*-tetrafluoroindazole[4a] yield hydrotris(indazolyl)borates with **a**-type structures regardless of the counterion. The new thallium complexes Tl[F12-Tp^{4Bo,3Ph}] (**Tl-1**), Tl[F12-Tp$^{4Bo,3(3,5\text{-}Me2C6H3)}$] (**Tl-3**), Tl[F30-Tp$^{4Bo,3(3,5\text{-}(CF3)2C6H3)}$] (**Tl-4**) were obtained from an excess of the appropriate aryl-1*H*-tetrafluoroindazole and most conveniently $TlBH_4$ instead of the more conventional KBH_4 in 72, 77, and 62% yield, respectively (Scheme 2).[16] The synthesis of Tl[F27-Tp^{4Bo,3C6F5}] (**Tl-2**) is discussed in the next section. ^{11}B NMR yielded a single broad signal around δ −3. ^{1}H and ^{19}F NMR solution spectra for these compounds show a single set of signals pointing to an overall C_{3v} symmetry in solution.

The X-ray structures of **Tl-1**, **Tl-3**, and **Tl-4** confirm that an **a**-type structure is adopted as expected (Figure 4). Tl–N, B–N bonds and N–Tl–N angles are virtually equal, except for **Tl-1** where N–Tl–N angles vary more than 10° (Table 1). All of them are unexceptional.[17] The structures are distorted from idealized C_{3v}, C_s, or C_3 symmetries. Apart from dihedral angles about the connection at C-3, the distortion mainly concerns the coordination to thallium (Table 1: torsion angles: B–N–N–Tl). Complex **Tl-3** appears to be the least distorted. For all complexes, each indazolyl ring is not coplanar with the corresponding mean B–N–N–Tl plane, a situation particularly noteworthy for one of the ring (Figure 4; Table 1: torsion angle B–N–N–C following the order: B1–N2–N1–C3, B1–N4–N3–C16, B1–N6–N5–C29). Complex **Tl-1** exhibits a close intramolecular F···F contact of 2.81 Å between F6 and F32, both 7-F of N1N2 and N5N6 based indazolyl groups. These distorted structures are probably due to an interplay between steric and packing effects.

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The packing of these thallium complexes is mainly dictated by aromatic type interactions whether they concern fluorinated rings, hydrogenated rings, or rings containing nitrogens and fluorines as analyzed in the literature.[1,11,13,17c]

Synthesis and Characterization of Complex Tl-2. When an excess of 3-pentafluorophenyl-4,5,6,7-tetrafluoro-1*H*-indazole (**2**) is reacted with $TlBH_4$ in the melt at about 200 °C, TlHB(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-1-yl)$_2$(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-2-yl) Tl[F27-Tp$^{(4Bo,3C6F5)*}$] (**Tl-2**) is formed and is isolated in 65% yield (Scheme 3).

Careful examination of crude reaction mixtures by ^{19}F NMR showed no other regioisomer was present at all stages of the reaction. The ^{19}F NMR data clearly point to an overall C_s structure in solution with two sets of resonances in a 2:1 ratio for each type of fluorine, including those from the C_6F_5 rings (viz. for F-5 fluorines with respect to boron: δ −167.18 (pt, 2F, *J* 19.2 Hz, F-5 *syn*), −152.32 (pt, 1F, *J* 16.9 Hz, F-5 *anti*). Also, no isomerization was observed upon heating pure **Tl-2** in anisole at 453 K for 8 h as ascertained by ^{19}F NMR. X-ray diffraction reveals that **Tl-2** (as its MeOH solvate **Tl-2.MeOH** in the crystal) indeed has the first **d**-type structure ever reported (Figure 5). It has been verified that redissolving the crystals gave the same ^{19}F NMR spectrum confirming that neither the crystallization process nor the presence of MeOH in the crystals induced any rearrangement or isomerization.

Figure 5. ORTEP drawing of Tl-F27-Tp$^{(4Bo,3C6F5)*}$·MeOH **Tl-2·MeOH**. Relevant bond lengths (Å) and angles (deg): N1−Tl1 2.659(4), N3−Tl1 2.623(4), N5−Tl1 2.837(4), N2−B1 1.535(6), N4−B1 1.555(6), N6−B1 1.531(7); N5−Tl1−N3 69.58(11), N5−Tl1−N1 67.47(12), N3−Tl1−N1 70.44(12), N6−B1−N4 108.8(4), N6−B1−N2 112.1(4), N4−B1−N2 110.3(4).

As can be seen from Figure 5, two indazolyl groups (N1N2 and N5N6) are bound to boron via their *N*1-nitrogen (N2 and N6) with C_6F_5 rings *syn* to the thallium. The third indazolyl group which contains N3 is "inverted", that is, bound to boron via its *N*2-nitrogen, N4 thereby directing the C_6F_5 ring *syn* to the boron. The B−N bond with this "inverted" indazole is barely longer than the other two (1.56 vs 1.53 Å). The C_6F_5 group of the "inverted" indazolyl group (torsional angle of 67°) is almost parallel to one of the indazolyl groups, that containing N1 and N2 (angle between planes 8°). The closest intramolecular contact between fluorines is that between F10 and F26 (2.78 Å), that is, F-7 on one indazolyl ring and an *ortho* fluorine of this inverted C_6F_5 ring, respectively.

To get a better insight into this regiochemistry issue, the relative stability of different isomers, most prominently those of **a**- and **d**-type, has been probed by a density functional theory (DFT) analysis. At the PBE1PBE/SDD/6-31G(d) level, the optimized **d**-type structure **Tl-2-d** (Figure 6) does not show the long Tl1−N5 bond as in the solid state where a cocrystallized methanol molecule interacts with the thallium. Apart from this particular Tl−N bond, calculated bond lengths and angles including those to Tl matched the experimental ones. The relative orientation of the "inverted" C_6F_5 ring with respect to the benzo rings is very similar to that observed in the solid state with the "inverted" C_6F_5 ring being almost parallel to one indazolyl group. The optimized structure of hypothetical **Tl-2-a** (Figure 6b) is very close in energy (+1.5 kJ.mol^{-1}) to that of **Tl-2-d** (Figure 6a) suggesting that there is little, if any, thermodynamic preference for the one or the other. This suggests that the exclusive formation of **Tl-2** with a **d**-type structure is most probably kinetically driven, and that the barrier linking **a**- and **d**-type isomers is very high since **Tl-2** does not rearrange upon heating (see above). Hypothetical **b**- and **c**-type isomers were also optimized (see Supporting Information) and their computed energies (relative to **Tl-2-d**), **Tl-2-b** (+0.8 kJ.mol^{-1}) and **Tl-2-c** (+2.5 kJ.mol^{-1}), are again very close, reinforcing the idea that kinetics, not thermodynamics, play a key role in the selective synthesis of **Tl-2**. It is noteworthy that **Tl-2-b,** despite having three bulky pentafluorophenyl groups *syn* to the boron, is the second most stable isomer after **Tl-2-d**. Similarly, none of these structures appear notably distorted. A larger energy difference (9 kJ.mol^{-1}) favoring **Tl-1** (i.e., **Tl-1-a**) over hypothetical **Tl-1-d** was computed.

Synthesis and Characterization of a Bis(indazolyl)-borate Thallium Complex. In an effort to probe the origin of the regiochemistry of **Tl-2** we decided to look at its stepwise synthesis by first preparing the bis(indazolyl)borate thallium compound. Surprisingly the perfluorinated bis(indazolyl)borate complex isolated in 74% yield (Scheme 4), is TlH_2B(3-pentafluorophenyl-4,5,6,7-tetrafluoroindazol-2-yl)$_2$ Tl[F18-Bp^{3Bo,5C6F5}] (**Tl-5**) which indeed has the two indazolyl substituents *syn* to the boron (Figure 7). ^{11}B NMR shows a single signal at δ −8.8, shielded as compared to those for Tl[Fn-Tp^{4Bo,R}] (see above).

The two indazolyl rings are symmetrically bound to the thallium. There is a weak B1−H1b···Tl1 agostic interaction (Tl···H 3.11, Tl···B 3.53 Å)[18] with a longer Tl···H distance than for the intermolecular interaction B1′-H1b′···Tl1 (Tl···H = 2.68, Tl···B = 3.55 Å) between two repeating units. The coordination at the thallium is supplemented by π-type interactions with a neighboring molecule (Tl···centroid N1.N2, 3.37; Tl···N1, 3.28; Tl···N2, 3.49; Tl···C1, 3.28 Å), and numerous F···F and CF···aromatic short contacts.

Monitoring the synthesis of **Tl-2** by ^{19}F NMR only showed excess 3-pentafluorophenyl-4,5,6,7-tetrafluoro-1*H*-indazole **2** and **Tl-5** *before* the third equivalent of indazole reacts. This confirms that complex rearrangements in the form of multiple B−N bond cleavage/formation events take place in this chemistry. Also, it is remarkable that a given connection between an indazolyl ring and boron might well show different preferences in bis or tris(indazolyl)borates. Even though we have no mechanistic information, it is gratifying that single isomers are obtained in all cases.

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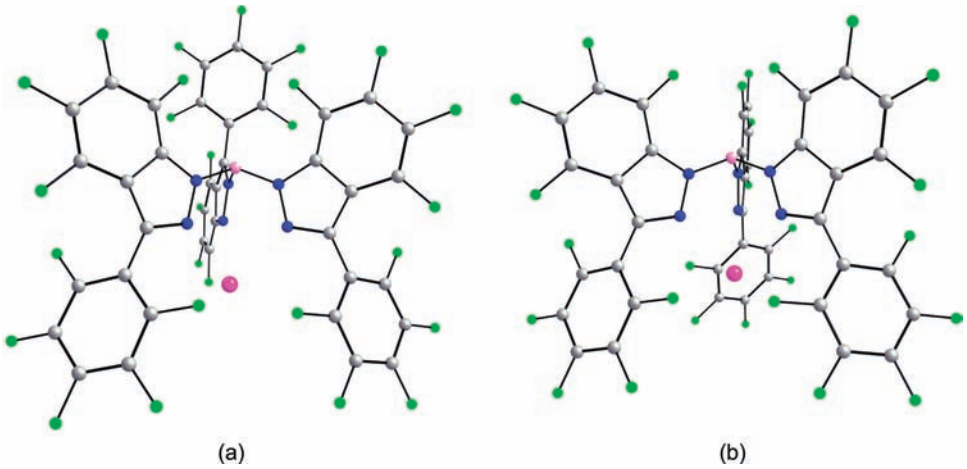
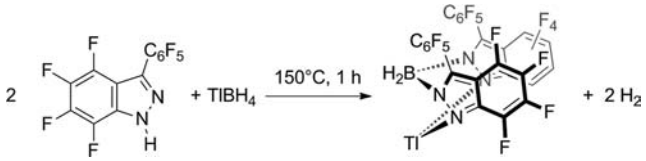


Figure 6. DFT optimized structures of **Tl-2-d** (a) and **Tl-2-a** (b). Color code: dark gray, C; blue, N; green, F; pink, B; purple, Tl; H omitted for clarity.

Scheme 4. Synthesis of Tl[F18-Bp^{3Bo,5C6F5}] (Tl-5)



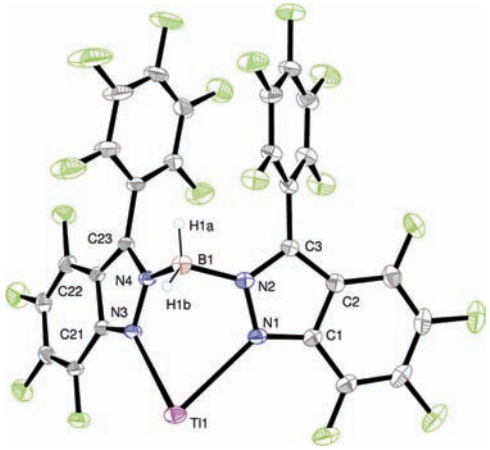


Figure 7. Molecular view **Tl-5**. Relevant bond lengths (Å) and angles (deg): N1−Tl1 2.706(3), N3−Tl1 2.688(3), N2−B1 1.548(6), N4−B1 1.555(5); N3−Tl1−N1 73.30(9), N4−B1−N2 109.5(3).

CONCLUSION

We have described the syntheses and characterization in solution and in the solid state of several highly fluorinated indazoles and indazolylborates. While phenyl, dimethylphenyl, and bis(trifluoromethyl)phenyl substituents yield hydrotris(indazolyl)borates of the type Tl[Fn-Tp^{4Bo,R}] with overall C_{3v} symmetry as expected, the use of the pentafluorophenyl substituent yields Tl[F27-Tp$^{(4Bo,3C6F5)}$*], a complex with overall C_s symmetry that has one indazolyl group bound to B via its N-2 nitrogen for the first time. While the cause of this particular behavior remains unclear, it is noted that the corresponding bis(indazolyl)borate, on the way to Tp$^{(4Bo,3C6F5)}$*, has both rings bound via N-2 demonstrating that reversible B−N bond cleavage is facile in certain circumstances. We now have in hands a range of highly fluorinated poly(indazolyl)borates for which we can tune the steric and electronic properties. We have already started to explore their utilization as ligands, particularly in the field of alkane functionalization,[4] and there is no doubt they will complement the growing family of highly fluorinated poly(azolyl)borates.[3]

EXPERIMENTAL SECTION

All experiments were performed using conventional vacuum line and Schlenk tube techniques or in a drybox under argon. Pentafluorobenzophenone, perfluorobenzophenone, methyl 3,5-dimethylbenzoate were purchased from Aldrich and methyl 3,5-bistrifluoromethylbenzoate from Fluorochem. The fluorinated indazoles were prepared according to a procedure used for the synthesis of 3-trifluoromethyl-4,5,6,7-tetrafluoroindazole[9] and following slight modifications to recently published procedures for **1** and **2**.[10] Thallium borohydride ($TlBH_4$) was prepared according to a published procedure.[16] NMR experiments were run on a Bruker DPX-300 MHz spectrometer (^{1}H, 300.13; ^{19}F, 282.40; ^{11}B, 96.25 MHz). Elemental analyses were performed in the Analytical Service of our Laboratory. Mass spectroscopic data were recorded on a QTRAP Applied Biosystems mass spectrometer.

3-Phenyl-4,5,6,7-tetrafluoro-1*H*-indazole (1). Pentafluorobenzophenone (4.00 g, 14.7 mmol) was dissolved in toluene (20 mL) and cooled down to 0 °C. Hydrazine monohydrate (715 μL, 14.7 mmol) was then added dropwise, and the mixture was stirred for 1 h at low temperature. The reaction mixture was then heated to reflux for 24 h, yielding a white mixture with a yellow aqueous phase. The phases were separated, and the aqueous phase was extracted with toluene (3 × 10 mL). The combined organic phases were dried over $MgSO_4$, and all volatiles were removed under vacuum, yielding a white solid that was purified by sublimation under vacuum (ca 140 °C). The white crystals were identified as 3-phenyl-4,5,6,7-tetrafluoro-1*H*-indazole (**1**) (3.72 g, 14.0 mmol, 95%). ^{1}H NMR ($CDCl_3$): δ 11.5 (vbr, 1H, NH), 7.85−7.47 (m, 5H, C_6H_5). ^{19}F NMR ($CDCl_3$): δ −164.62 (ptd, 1F, J = 19.5, 2.8 Hz, F-5), −158.90 (pt, 1F, J = 18.6 Hz, F-7), −156.18 (pt, 1F, J = 19.2 Hz, F-6), −140.38 (pt, 1F, J = 18.6 Hz, F-4). Anal. Calcd for $C_{13}H_6F_4N_2$: C, 58.66; H, 2.27; N, 10.52. Found: C, 58.58; H, 1.75; N, 10.63.

3-Pentafluorophenyl-4,5,6,7-tetrafluoro-1*H*-indazole (2). Following the same procedure, perfluorobenzophenone (2.50 g, 6.90 mmol) and hydrazine monohydrate (335 μL, 6.90 mmol) yielded a white solid identified as 3-pentafluorophenyl-4,5,6,7-tetrafluoro-1*H*-indazole (**2**) (2.22 g, 90%). ^{1}H NMR (acetone-d_6): δ 10.72 (vbr, 1H, NH). ^{19}F NMR (acetone-d_6): δ −166.92 (ptd, J = 18.6, 2.2 Hz, 1F, F-5), −164.02 (m, 2F, *meta*-C_6F_5), −159.29 (pt, J = 18.4 Hz, 1F, F-7), −159.04 (ptd, J = 18.1, 2.3 Hz, 1F, F-6), −154.57 (pt, J = 20.6 Hz, 1F,

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F4), −150.84 (m, 1F, *para*-C_6F_5), −142.42 (m, 2F, *ortho*-C_6F_5). Anal. Calcd for $C_{13}HF_9N_2$: C, 43.84; H, 0.28; N, 7.87. Found: C, 43.48; H, 0.00; N, 8.62.

3-(3,5-Dimethylphenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (3). 3,5-Dimethylpentafluorobenzophenone was first synthesized following the reported procedure from commercially available methyl-3,5-dimethylbenzoate. Pentafluorobromobenzene (3.80 mL, 30.49 mmol) was dissolved in diethyl ether (10 mL) and cooled at −80 °C. *n*-Butyllithium (12.19 mL, 30.50 mmol), precooled to −80 °C, was added dropwise over a period of 20 min. The mixture was stirred for another 10 min at low temperature. After that time, a solution of methyl-3,5-dimethylbenzoate (5.01 g, 30.50 mmol) in diethyl ether (20 mL) was quickly added, and the reaction was stirred for 15 min, before being quenched with cold HCl (2N, 70 mL, 0 °C). The mixture was stirred overnight at room temperature. The two phases were separated, and the aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic phases were dried over $MgSO_4$ and all volatiles were removed under reduced pressure to yield a viscous colorless liquid, which was purified by column chromatography (CH_2Cl_2-hexane 1:5). The resulting white solid 3,5-dimethylpentafluorobenzophenone (4.84 g, 16.1 mmol) was used without further purification for the subsequent cyclization step in the usual manner. 3,5-Dimethylpentafluorobenzophenone (4.84 g, 16.1 mmol) and hydrazine monohydrate (0.79 mL, 16.3 mmol) yielded white crystals identified as 3-(3,5-dimethylphenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (**3**) (3.31 g, 37%). ^{1}H NMR (acetone-d_6): δ 13.61 (vbr, 1H, NH), 7.50 (s, 2H, *ortho*-$C_6H_3Me_2$), 7.13 (s, 1H, *para*-$C_6H_3Me_2$), 2.40 (s, 6H, $C_6H_3Me_2$). ^{19}F NMR (acetone-d_6): δ −168.76 (pt, J = 19.2 Hz, 1F, F-5), −160.94 (pt, J = 19.2 Hz, 1F, F-7), −160.56 (pt, J = 19.2 Hz, 1F, F-6), −142.65 (pt, J = 19.2 Hz, 1F, F-4). Anal. Calcd for $C_{15}H_{10}F_4N_2$: C, 61.23; H, 3.43; N, 9.52. Found: C, 58. 91; H, 2.92; N, 9.54.

3-(3,5-Bis(trifluoromethyl)phenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (4). Following the same procedure detailed for **3**, 3-(3,5-bis(trifluoromethyl)phenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (**4**) was obtained from the commercially available methyl-3,5-bis-(trifluoromethyl)benzoate (yield: 83%). ^{1}H NMR ($CDCl_3$): δ 10.78 (vbr, 1H, NH), 8.41 (s, 2H, *o*-$C_6H_3(CF_3)_2$), 7.98 (s, 1H, *p*-$C_6H_3(CF_3)_2$). ^{19}F NMR ($CDCl_3$): δ −162.60 (pt, J = 19.5 Hz, 1F, F-5), −158.00 (pt, J = 18.6 Hz, 1F, F-7), −154.60 (pt, J = 19.2 Hz, 1F, F-6), −139.95 (pt, J = 18.9 Hz, 1F, F-4), −63.03 (s, 6F, CF_3). Anal. Calcd for $C_{15}H_4F_{10}N_2$: C, 44.79; H, 1.00; N, 6.97. Found: C, 43.21; H, 0.96; N, 6.12.

Tl[F_{12}-$Tp^{4Bo,3Ph}$] (Tl-1). Two procedures were used to synthesize **Tl-1**.

(1) A mixture of 3-phenyl-4,5,6,7-tetrafluoroindazole (**1**) (2.0 g, 7.50 mmol) and $TlBH_4$ (0.484 g, 2.21 mmol) was heated up to 180 °C for 2 h. The reaction mixture was allowed to cool to room temperature. The residue was washed with a methanol/pentane (1/5) mixture. Tl[F_{12}-$Tp^{4Bo,3Ph}$] (**Tl-1**) was obtained as a white powder after drying under vacuum (1.84 g, 1.82 mmol, 82%). Anal. Calcd for $C_{39}H_{16}BF_{12}N_6Tl$: C, 46.30; H, 1.59; N, 8.31. Found: C, 46.45; H, 1.53; N, 8.71. ESI-MS: m/z (relative intensity) 807.5 (100, M^-), 205 (100, M^+).

(2) KBH_4 was first dried at 140 °C under vacuum for 1 h. KBH_4 (0.12 g, 2.2 mmol) and 3-phenyl-4,5,6,7-tetrafluoroindazole (**1**) (2.0 g, 7.5 mmol) were introduced in a Schlenk tube. The mixture was heated up to 190 °C for 4 h. The reaction mixture was allowed to cool to room temperature and excess **1** was removed by vacuum sublimation at 170 °C. The grayish residue was washed with methanol and dried under vacuum. K[F_{12}-$Tp^{4Bo,3Ph}$] was obtained as a white powder (1.40 g, 1.65 mmol, 75%). [^{1}H NMR (acetone-d_6): δ 7.72−7.25 (m, 15H, 3×C_6H_5). ^{19}F NMR (acetone-d_6):δ −171.55 (pt, 1F, J = 19.8 Hz, F-5), −165.34 (pt, 1F, J = 19.5 Hz, F-7), −155.91 (m, 1F, F-6), −145,02 (pt, 1F, J = 18.6 Hz, F-4). IR: ν(B−H)= 2554 cm^{-1}. ^{11}B NMR (acetone-d_6): δ −2.26. ESI-MS: m/z (relative intensity) 807.5 (100, M^-)]. A solution of thallium(I) sulfate (0.223 g, 0.44 mmol) in water (50 mL) was then added to a solution of K[F_{12}-$Tp^{4Bo,3Ph}$] (0.50 g, 0.59 mmol) in chloroform (50 mL). The mixture was stirred vigorously for 24 h. By that time solid Tl_2SO_4 had disappeared. The organic layer was then decanted, and the water extracted with chloroform (2 × 10 mL). After the evaporation of the combined organic phases, a white powder of Tl[F_{12}-$Tp^{4Bo,3Ph}$] (**Tl-1**) (0.42 g, 0.41 mmol) was obtained in 68% yield. Anal. Calcd for $C_{39}H_{16}BF_{12}N_6Tl$: C, 46.30; H, 1.59; N, 8.31. Found: C, 45.74; H, 1.02; N, 8.29.

Tl[F27-$Tp^{(4Bo,3C6F5)*}$] (Tl-2). A mixture of 3-pentafluorophenyl-4,5,6,7-tetrafluoroindazole (**2**) (1.00 g, 2.81 mmol) and $TlBH_4$ (0.17 g, 0.78 mmol) was heated up to 200 °C for 4 h. The reaction mixture was allowed to cool to room temperature. Excess **2** was removed by vacuum sublimation at 140 °C. Tl[F_{27}-$Tp^{4Bo,3C6F5}$] (**Tl-2**) was obtained as a white powder (0.65 g, 0.51 mmol, 65%). ^{19}F NMR (acetone-d_6): δ −167.18 (pt, 2F, J = 19.2 Hz, F5 *syn*), −166.17 (pt, 1F, J = 16.9 Hz, F6 *anti*), −164.08 (m, 2F, *meta*-C_6F_5 *anti*), −163.58 (m, 4F, *meta*-C_6F_5 *syn*), −161.08 (pt, 1F, J = 16.9 Hz, F7 *anti*), −159.57 (pt, 2F, J = 18.6 Hz, F6 *syn*), −155.70 (m, 1F, F4 *anti*), 155.42 (m, 2F, F7 *syn*), −154.51 (pt, 2F, J = 20.6 Hz, *para*-C_6F_5 *syn*), −152.89 (m, 1F, *para*-C_6F_5 *anti*), −152.32 (pt, 1F, J = 16.9 Hz, F5 *anti*), −151.94 (pdt, 2F, J = 22.0, 9.3 Hz, F4 *syn*), −141.24 (m, 4F, *ortho*-C_6F_5 *syn*), −139.29 (pd, 2F, J = 21.2 Hz, *ortho*-C_6F_5 *anti*). ^{11}B NMR (acetone-d_6): δ −3.15. Anal. Calcd for $C_{39}HBF_{27}N_6Tl$: C, 36.55; H, 0.08; N, 6.56. Found: C, 36.14; H, 0.00; N, 7.65. ESI-MS: m/z (relative intensity) 1077.6 (100, M^-), 205 (100, M^+).

Tl[F_{12}-$Tp^{4Bo,3(3,5-Me2C6H3)}$] (Tl-3). A mixture of 3-(3,5-dimethylphenyl)-4,5,6,7-tetrafluoro-1*H*-indazole (**3**) (0.50 g, 1.70 mmol) and $TlBH_4$ (0.11 g, 0.50 mmol) was heated up to 210 °C for 4 h. The reaction mixture was allowed to cool to room temperature. The residue was washed with pentane. **Tl-3** was obtained as a white powder (0.42 g, 0.38 mmol, 77%). ^{1}H NMR (acetone-d_6): δ 7.31 (s, 6H, *ortho*-$C_6H_3Me_2$), 7.13 (s, 3H, *para*-$C_6H_3Me_2$), 2.34 (s, 18H, $C_6H_3Me_2$). ^{19}F NMR (acetone-d_6): δ −168.81 (pt, J = 19.8 Hz, 1F, F-5), −160.16 (pt, J = 18.6 Hz, 1F, F-7), −154.56 (m, 1F, F-6), −145.52 (pt, J = 19.2 Hz, 1F, F-4). ^{11}B NMR (acetone-d_6): δ −2.67. Anal. Calcd for $C_{45}H_{28}BF_{12}N_6Tl$: C, 49.32; H, 2.58; N, 7.67. Found: C, 51.21; H, 1.89; N, 8.33. DCI-MS: m/z 1097.2 $[M + H]^+$. High resolution LSI calculated $[M + H]^+$: 1096.2 ($C_{45}H_{28}BF_{12}N_6Tl$). Found 1096.2 (100% $[M + H]^+$).

Tl[F_{12}-$Tp^{4Bo,3(3,5-(CF3)2C6H3)}$] (Tl-4). A mixture of 3-(3,5-bis-(trifluoromethyl)phenyl)-4,5,6,7-tetrafluoroindazole (**4**) (1.10 g, 2.73 mmol) and $TlBH_4$ (0.19 g, 0.85 mmol) was heated up to 180 °C for 5 h. The reaction mixture was allowed to cool to room temperature. The residue was sublimated at 140 °C to remove unreacted **4**. Tl[F_{30}-$Tp^{4Bo,3(3,5(CF3)2C6H3)}$] (**Tl-4**) was obtained as a white powder (0.75 g, 0.53 mmol, 62%). ^{1}H NMR ($CDCl_3$): 8.01 (s, 9H, $C_6H_3(CF_3)_2$). ^{19}F NMR ($CDCl_3$): δ −162.45 (pt, J = 19.6 Hz, 1F, F-5), −153.34 (pt, J = 18.10 Hz, 1F, F-7), −151.20 (m, 1F, F-6), −144.33 (pt, J = 18.8 Hz, 1F, F-4), −63.26 (s, 6F, $C_6H_3(CF_3)_2$). ^{11}B NMR ($CDCl_3$): δ −2.98. Anal. Calcd for $C_{45}H_{10}BF_{30}N_6Tl$: C, 38.07; H, 0.71; N, 5.92. Found: C, 38.78; H, 0.00; N, 6.34. ESI-MS: m/z (relative intensity) 1215.4 (100, M^-), 205 (100, M^+).

Tl[F_{18}-$Bp^{3Bo,3C6F5}$] (Tl-5). A mixture of 3-pentafluorophenyl-4,5,6,7-tetrafluoroindazole (**2**) (0.50 g, 1.40 mmol) and $TlBH_4$ (0.15 g, 0.70 mmol) was heated up to 150 °C for 1 h. The reaction mixture was allowed to cool to room temperature. The residue was washed with a pentane/toluene (3/1) mixture. Tl[F_{18}-$Bp^{4Bo,3C6F5}$] (**Tl-5**) was obtained as a white powder (0.48 g, 0.52 mmol, 74%). ^{19}F NMR (acetone-d_6): δ −167.96 (pt, J = 17.4 Hz, 2F, F-5), −164.61 (m, 4F, *meta*-C_6F_5), −163.32 (pt, 2F, J = 16.9 Hz, F-7), −156.61 (pt, 2F, J = 18.2 Hz, F-6), −154.48 (pt, 2F, J = 20.2 Hz, F-4), −153.32 (pt, 2F, J = 18.8 Hz, *para*- C_6F_5), −138.87 (pd, 4F, J = 19.8 Hz, *ortho*-C_6F_5). ^{11}B NMR (acetone-d_6): δ −8.8. Anal. Calcd for $C_{26}H_2BF_{18}N_4Tl$: C, 33.63; H, 0.22; N, 6.04. Found: C, 34.54; H, 0.00; N, 6.91. ESI-MS: m/z (relative intensity) 723.5 (100, M^-), 205 (100, M^+).

X-ray Crystallography. Data for **1**, **2**, **4**, **Tl-1**, **Tl-2·MeOH**, **Tl-4**, **Tl-5** were collected at 180 K on an Xcalibur Oxford Diffraction diffractometer equipped with an Oxford Instrument Cooler Device. Data for **Tl-3** were collected at 180 K on a Bruker Kappa Apex II diffractometer equipped with an Oxford Cryosystems Cryostream

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Table 2. Crystal Data, Data Collection, and Refinement for Compounds 1, 2, 4, Tl-1, Tl-2·MeOH, Tl-3, Tl-4

	1	2	4	Tl-1	Tl-2·MeOH	Tl-3	Tl-4
formula	$C_{13}H_6F_4N_2$	$C_{13}HF_9N_2$	$C_{15}H_4F_{10}N_2$	$C_{39}H_{16}BF_{12}N_6Tl$	$C_{40}H_5BF_{27}N_6OTl{\cdot}CH_4O$	$C_{45}H_{28}BF_{12}N_6Tl$	$C_{45}H_{10}BF_{30}N_6Tl$
formula weight	266.20	356.16	402.20	1011.76	1345.72	1095.91	1419.77
temperature/K	180	180	180	180	180	180	180
λ (MoKα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	triclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$Pbc2_1$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.0480(5)	3.81860(10)	12.6031(10)	11.9370(6)	11.8175(3)	11.2334(8)	20.5920(4)
b/Å	14.0810(8)	12.3676(3)	7.5208(6)	11.9610(6)	13.9013(3)	13.2250(11)	21.8080(5
c/Å	21.7250(14)	13.7752(4)	15.6167(15)	14.4060(7)	14.9703(4)	15.366(2)	11.1760(2)
α/deg	90	67.237(3)	90	104.020(4)	110.435(2)	104.709(3)	90
β/deg	90	82.115(2)	109.848(10)	110.394(4)	99.598(2)	96.815(6)	94.027(2)
γ/deg	90	89.001(2)	90	103.113(4)	104.244(2)	100.048(5)	90
V/Å^3	2156.1(2)	593.77(3)	1392.3(2)	1757.50(15)	2145.53(11)	2142.0(4)	5006.42(18)
Z	8	2	4	2	2	2	4
ρ_{calcd}/Mg m^{-3}	1.640	1.992	1.919	1.912	2.083	1.699	1.884
μ/mm^{-1}	0.148	0.22	0.209	4.700	3.93	3.863	3.379
F(000)	1072	348	792	972	1284	1068	2712
crystal size/mm	0.2 × 0.15 × 0.05	0.25 × 0.15 × 0.03	0.2 × 0.15 × 0.05	0.19 × 0.12 × 0.07	0.3 × 0.2 × 0.08	0.2 × 0.12 × 0.03	0.25 × 0.15 × 0.08
θ range/deg	2.89−26.36	3.58−25.68	2.72−24.71	2.61−26.37	2.66−25.35	2.13−32.1	2.72−26.37
index range	$-8 \le h \le 8$	$-4 \le h \le 4$	$-14 \le h \le 14$	$-14 \le h \le 14$	$-14 \le h \le 14$	$-16 \le h \le 16$	$-25 \le h \le 17$
	$-13 \le k \le 17$	$-15 \le k \le 15$	$-8 \le k \le 8$	$-14 \le k \le 14$	$-16 \le k \le 16$	$-19 \le k \le 19$	$-27 \le k \le 27$
	$-27 \le l \le 27$	$-16 \le l \le 16$	$-14 \le l \le 18$	$-15 \le l \le 18$	$-18 \le l \le 17$	$-22 \le l \le 21$	$-13 \le l \le 13$
reflections collected/ unique	15734/2262, R(int) = 0.0692	11765/2253, R(int) = 0.0184	9132/2373, R(int) = 0.0323	12062/6924, R(int) = 0.1092	15000/7809, R(int) = 0.0254	64621/14857, R(int) = 0.0367	38754/10217, R(int) = 0.0317
completeness to θ/derg	26.36 (100%)	25.68 (99.7%)	24.71 (100.0%)	26.37 (96.5%)	25.35 (99.5%)	32.1 (99.1%)	26.37 (99.9%)
absorption corrections	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max/min transmission	0.989/0.975	0.997/0.906	0.987/0.96	0.715/0.41	0.725/0.408	0.888/0.592	0.748/0.561
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	2262/1/343	2253/1/220	2373/0/241	6924/0/532	7809/0/707	14857/0/592	10217/0/748
goodness-of-fit on F^2	0.983	1.141	1.128	1.135	1.034	1.006	1.064
final R indices $I > 2\sigma(I)$	R1 = 0.0620	R1 = 0.027	R1 = 0.0694	R1 = 0.0311	R1 = 0.035	R1 = 0.0283	R1 = 0.0299,
	wR2 = 0.1506	wR2 = 0.081	wR2 = 0.1742	wR2 = 0.0680	wR2 = 0.0873	wR2 = 0.058	wR2 = 0.0780
R indices (all data)	R1 = 0.0766	R1 = 0.0323	R1 = 0.0964	R1 = 0.0568	R1 = 0.0421	R1 = 0.0383	R1 = 0.0425
	wR2 = 0.1606	wR2 = 0.083	wR2 = 0.1881	wR2 = 0.0884	wR2 = 0.0908	wR2 = 0.0602	wR2 = 0.0812
largest diff. peak/hole/Å^3	0.751/−0.318	0.241/−0.168	1.128/−0.867	1.847/−1.857	1.539/−0.842	0.817/−0.837	1.210/−0.739

Cooler Device. Details of crystal data, data collection, and refinement can be found in Table 2. The structures have been solved by direct methods using SHELXS-86[19] for **Tl-1**, SHELXS-97[19] for **4**, and SIR92[20] for all other compounds. The structures were refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[18] included in the software package WinGX version 1.63.[21] The Atomic Scattering Factors were taken from the International Tables for X-ray Crystallography.[22] All hydrogen atoms were geometrically placed and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights were calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Plots of the molecular structures were performed with the programs ORTEP32[23] or CAMERON[24] with 30% probability displacement ellipsoids for non-hydrogen atoms.

For compounds **Tl-3**, it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecule). Treatment with the SQUEEZE facility from PLATON[25] resulted in a smooth refinement. Since a few low order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for D(calc), F(000), and the molecular weight are only valid for the ordered part of the structure. Even if the best possible crystal has been sought and utilized for the data collection and even if the data were collected at low temperature, compound **4** was weakly diffracting. As a result, there is a low sine(θ_max)/wavelength (0.59), and a poor data/parameter ratio. Moreover, the overall quality of the data being poor, this leads to spurious peaks and holes of residual electron density. Compound **Tl-4** presents highly disordered fluorines.

Computational Details. All DFT calculations were performed with Gaussian03.[26] Structures were optimized at the PBE1PBE level.[27] The thallium was described with the Stuttgart/Dresden ECP valence basis set and the quasi-relativistic effective core potential of Kuchle et al.[28] The 6-31G(d) basis was used for F, N, C, B, and H.[29] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the *extrema* (*minima*) was verified with analytical frequency calculations (no imaginary frequency).

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■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF files), detailed packing analyses, full ref 26, and computational details (Cartesian coordinates and absolute energies of optimized structures). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michel.etienne@lcc-toulouse.fr.

Notes

The authors declare no competing financial interest.

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