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Perfluorinated 1*H*-indazoles and hydrotris(indazol-1-yl)borates. Supramolecular organization and a new synthetic procedure to scorpionate ligands.

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Abstract. This paper describes the syntheses and full characterization of perfluorinated 1*H*-indazoles **2-5** and hydrotris(indazolyl)borate thallium complexes **6-9** that contain linear perfluoroalkyl chains varying between two to six carbon atoms in the 3-position. In the solid state, the perfluorinated 1*H*-indazoles exhibit supramolecular structures that depend on the length of the perfluoroalkyl chain. A catemer of order 3 is observed with the CF_2CF_3 derivative **2** (chiral space group $P3_2$), catemers of order 2 are observed for the C_3F_7 and C_4F_9 derivatives **3** (chiral space group $P2_12_12_1$, one type of helix in the unit cell) and **4** (space group $P2_1/n$, two types of helices in the unit cell), respectively, and stacks of dimers are observed for the indazole with the longer C_6F_{13} chain **5** (space group $P2_1/c$). The perfluorinated hydrotris(indazolyl)borate thallium complexes **6-9** [TlFn-$Tp^{4Bo,3Rf}$] have been obtained by a new reaction based on the reaction of $HBBr_2$ (generated *in situ* from BBr_3 and Et_3SiH) with the indazolates of **2-5** followed by cation exchange. The X-ray crystal structure of [TlF_{33}-$Tp^{4Bo,3C3F7}$] **7** shows that, in addition to coordination to the three nitrogens, the thallium is buried in a nest of fluorines with seven short intramolecular Tl···F contacts with the pending perfluoropropyl chains. The potential of these highly fluorinated molecules as ligands is highlighted.

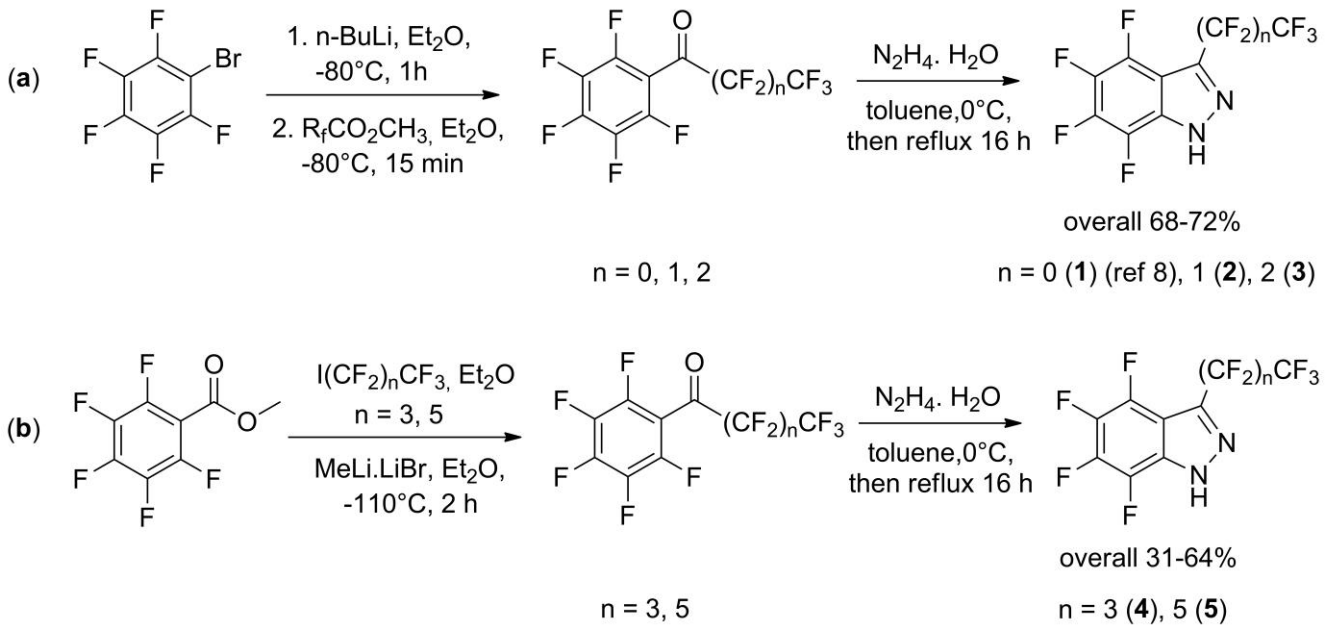
Introduction

Due to the unique properties of fluorine, the interest in highly fluorinated compounds in organic and inorganic chemistry with a wide range of applications in supramolecular, biochemical and materials chemistry and in catalysis continues unabated.[1] For example, fluorinated pyrazoles[2] and fluorinated hydrotris(pyrazolyl)borates (Tp') and some of their metal complexes[3] have been known for some time; the strong electron-withdrawing power of fluorinated substituents (*ie* CF_3 for example) imparts remarkable chemical properties ranging from very low pKa of the 1*H*-pyrazoles[4] to highly electrophilic Tp' metal complexes.[3] Indazoles (benzopyrazoles)[2] have interesting structural properties[5] and, when fluorinated, show unique biological properties,[6] but their use as building blocks for poly(indazolyl)borates in coordination chemistry is much less developed than that of pyrazoles.[2a,b,7] We have embarked on a research program devoted to highly fluorinated 1*H*-indazoles,[8] indazolates[9] and poly(indazolyl)borates.[10] Perfluorinated 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole 3-CF_3IndF_4H (**1**) crystallizes as a chiral infinite catemer of order 3.[8] The corresponding highly electron-poor scorpionates, hydrotris(3-trifluoromethyl-4,5,6,7-tetrafluoroindazolyl)borate F_{21}-$Tp^{4Bo,3CF3}$ and hydrotris(3-pentafluoroethyl-4,5,6,7-tetrafluoroindazolyl)borate F_{27}-$Tp^{4Bo,3CF2CF3}$, form Cu(I) and Ag(I) complexes that catalyze carbene (:$CHCO_2Et$ from ethyldiazoacetate) insertion into alkane CH bonds, including methane itself in the case of Ag(I).[10] Thanks to the fluorinated substituents, the Ag(I) catalysts are soluble in supercritical carbon dioxide that is used as the solvent in the case of methane. With longer 3-perfluoroalkyl chains Rf in F_n-$Tp^{4Bo,3Rf}$Ag(L), the catalysis proceeds in fluorinated solvents providing a recyclable system for alkane functionalization.[11] In this paper, we report a full account of the syntheses and characterization of the perfluoroalkyl substituted indazoles and thallium hydrotris(indazolyl)borates. The synthetic procedure for the 1*H*-indazoles depends on the length of Rf (Rf = C_nF_{2n+1}, n = 2, 3, 4, 6). Depending on n, their supramolecular structures in the solid state vary from dimers (n = 6) to helices of order 2 (n = 3, 4) or 3 (n = 2). A new synthetic scheme based on nucleophilic substitutions at boron is also established for the corresponding hydrotris(indazolyl)borates.

Results and Discussion

We first describe the syntheses of the indazoles and the hydrotris(indazolyl)borates before discussing their characterization mainly by ^{19}F NMR and X-ray diffraction.

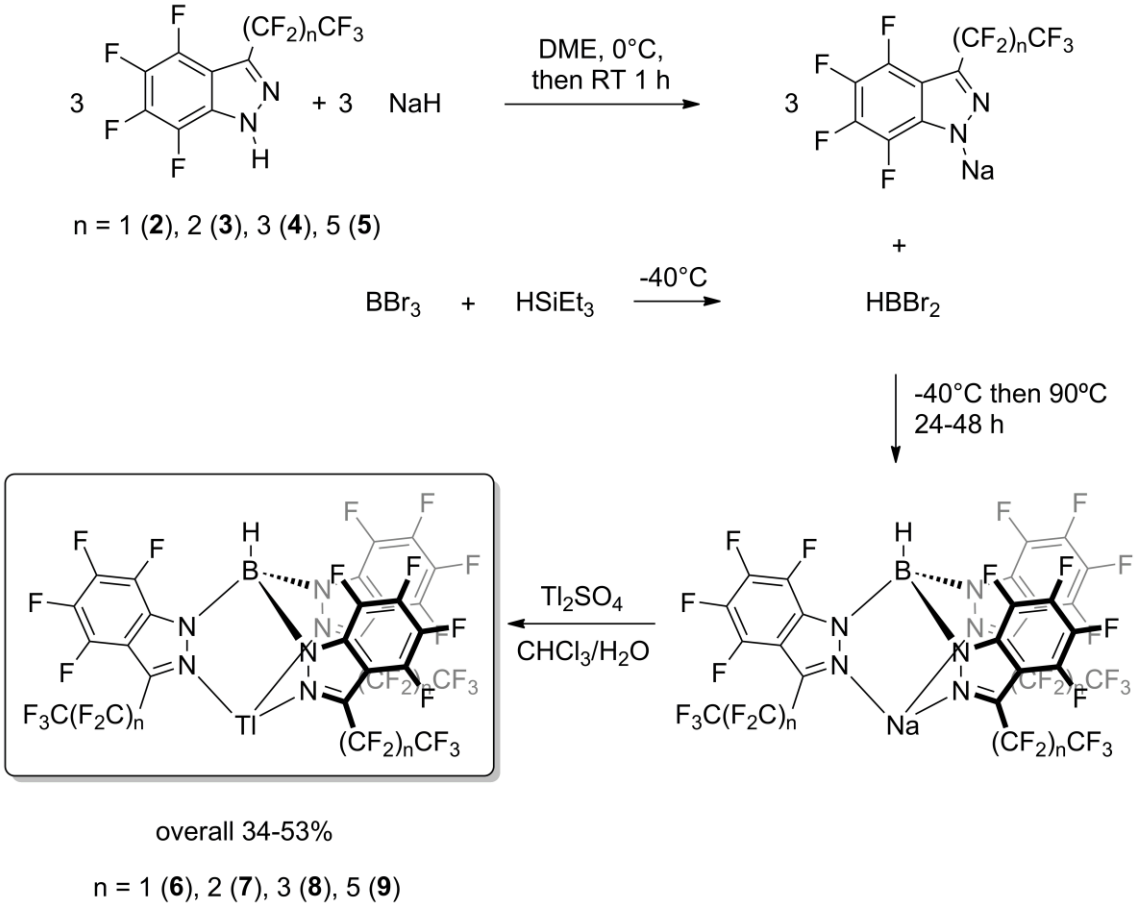
Synthesis of the perfluorinated 1*H*-indazoles. The indazoles **2** and **3** were synthesized following the procedure already reported for 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole[8] **1** showed in Scheme 1a, whereas the indazoles **4** and **5** were synthesized according to the procedure showed in Scheme 1b. The difference between the two methods lies on the ketone synthesis. In the first one (Scheme 1a), the nucleophilic substitution of the pentafluorophenyllithium on the perfluoroalkylmethylester controls the overall yield because a subsequent nucleophilic addition can occur affording the corresponding perfluoroalcohol [*ie* $(C_6F_5)_2(C_6F_{13})OH$]. The formation of this undesired by-product can be avoided by decreasing the reaction temperature. In Scheme 1b, the ketones are synthesized following a modification of the method reported by Gassman *et al*.[12] The perfluoroalkyl lithium is generated *in situ* and nucleophilic attack occurs on methylpentafluorobenzoate. This method is most efficient to introduce longer perfluorinated chains. The drawback however is that a large excess of the perfluoroalkyl iodide is required; the reaction was optimized with an ester/alkyl iodide ratio of 1:4.2. Using either method, the isolated yields of the ketones were in the range 80-95%. The indazoles were then obtained by reaction of the corresponding ketone with hydrazine monohydrate as previously reported for 3-trifluoromethyl-4,5,6,7-tetrafluoro-1*H*-indazole.[8] All indazoles were obtained in reproducible isolated yields from 60-80%. Only in the case of 3-tridecafluorohexyl-4,5,6,7-tetrafluoro-1*H*-indazole (**5**), a by-product of the substitution of the fluorine at the 6-position of the indazole by hydrazine was obtained. The formation of this by-product resulting from nucleophilic attack at the less hindered *para* position of the highly activated tridecafluorohexylpentafluorobenzoate is documented.[6b,13]



Scheme 1. Preparation of indazoles **2-5**.

Synthesis of the hydrotris(indazolyl)borates. We initially described the synthesis of M[F_{21}-$Tp^{4Bo,3CF3}$] (M = K, Tl) using a typical Trofimenko's method.[3a,3b,10a] The thallium complex was obtained in 27% yield by first heating the indazole at high temperatures (>180ºC) in the presence of KBH_4 followed by cation exchange. This classical procedure was tedious and/or gave even lower yields for other Rf. Other methods, more suited to the preparation of tetrasubstituted borato derivatives that use milder conditions were disappointing as well.[14] However, the idea of repeated nucleophilic substitutions and addition at boron was inspiring. The new perfluorinated F_n-$Tp^{4Bo,3Rf}$ anions were synthesized by the reaction of 3.1 equiv. of sodium indazolate (generated from the indazoles **2-5** (3.2 equiv) and NaH (3.1 equiv) in dimethoxyethane) with dibromoborane (generated *in situ* from boron tribromide and triethylsilane at -40ºC) as illustrated in Scheme 2. The thallium complexes were then obtained by cation exchange with thallium sulfate. Depending on the purification steps, the sodium salts are obtained in yields < 70%. The cation exchange works well for complexes **6-8** affording yields higher than 75%. For **9** the cation exchange yield was only 55%, due to the poorly efficient organic phase separation possibly due to the long ponytail properties. The overall isolated yields of the thallium complexes vary between

35 to 60% The thallium compounds **6-9** were characterized by C, H, N elemental analysis, mass spectrometry (ESI-MS), ^{19}F, ^{11}B and ^{13}C NMR and by an X-ray crystal structure for complex **7**.



Scheme 2. Synthetic procedure for the hydrotris(indazolyl)borates

^{19}F NMR characterization. ^{19}F NMR is the spectroscopic method of choice. ^{19}F NMR data of the indazoles **2-5** are collected in Table 1 and those for the tris(indazolyl)borates **6-9** in Table 2. For the indazoles, the signals corresponding to the aromatic fluorine atoms were assigned by comparison with those of **1**.[13] Second order splitting patterns for the perfluorinated chains were observed at room temperature as expected.[16] Indazoles **2-5** contain the same aromatic skeleton but differ in the pig/ponytails length. The pig or ponytails can adopt a helical twist or a zigzag conformation in solution and in some cases the ^{19}F NMR spectra can offer information about the structure. In particular the coupling constants are related to the geometry and bond angles of the molecule in solution. The four-bond coupling constants ($^4J_{FF}$), typically larger than a three-bond coupling constants ($^3J_{FF}$), for the CF_3

signal can be extracted from the spectra for indazoles **2-5**. These *J* values increase with the chain length ($^4J_{CF3CF2}$ = 9.6-10.2 Hz) as observed for perfluorocarboxylic acids.[15] A qualitative analysis of the ^{19}F NMR spectra recorded at room temperature shows multiplicity and well-defined signals for the pigtails contained in compounds **2-4**. These well-defined signals suggest that the perfluorocarbon chains up to C4 are flexible backbones. For the ponytail in **5** however, only broad signals are observed for all the CF_2's suggesting the C6 chain is more rigid probably due to steric hindrance and the multiple fluorine interactions. We have not synthesized indazoles with longer perfluorinated alkyl chain to confirm this dependence although a trend is definitely observed. This observation is also in agreement with that reported by comparison of the perfluorobutyric and perfluorooctanoic acids.[15] For the tris(indazolyl)borate thallium derivatives **6-9** (Table 2), the major changes in the ^{19}F NMR spectra are shifts to lower fields for the benzo fluorines with an effect most pronounced for F7. $^4J_{F4F6}$ is found to increase from *ca* 2 to *ca* 9-9.5 Hz. The signals for the perfluoroalkyl fluorines all become broader as expected upon Tl complexation.[16] Despite close Tl…F contacts (see X-ray structure below), no ^{19}F-^{203}Tl or ^{19}F-^{205}Tl coupling could be identified as for $TlTp^{(CF3)2}$ and contrary to $TlTp^{C3F7}$.[3h,k] Due to potential broadening of the NMR signals by thallium, a discussion of the rigidity of the fluorinated chains is precluded for the thallium complexes.

X-Ray crystal structures.

Indazoles. The crystal and refinement data for indazoles **2-5** are shown in Table 3 Indazoles **2-5** crystallized in different hexagonal, orthorhombic and monoclinic systems. The distances and angles observed for the 1*H*-indazole skeleton are very similar, including those involving the atoms directly attached to the perfluoroalkyl tails. The numbering scheme follows the IUPAC rules for the indazole skeletons. The characteristic distances C(3)-N(2) and angles C(3)-N(2)-N(1) for **2**, **3**, **4** and **5** are all very similar at 1.322(9), 1.327(2), 1.319(3), 1.318(4) Å and 107.2(6), 106.31(14), 106.69(16), 105.9(3)º, respectively. These values are also very close to those obtained for indazole **1** bearing a trifluoromethyl group in position 3.[8] Interestingly different supramolecular structures are observed for **2-5**. A schematic view of these structures is presented Figure 1. The compounds **2**, **3** and **4** form catemers of orders 3 for **2**

(Figure 2) and 2 for **3** and **4** (Figures 3 and 4), while the indazole **5** bearing the longest perfluorinated chain form dimers (Figure 5). Recall that indazole **1** forms a helical catemer of order 3.[8] According to Foces-Foces and Gonzalez,[5a,b] 1*H*-indazoles crystallize either as cyclic dimers, cyclic trimers or catemers of order 2 or 3. Depending on the perfluoroalkyl chain length in **2-5** all these supramolecular structures but the cyclic trimers are observed here. Although devoid of stereogenic center catemer **2**, just like **1**, crystallizes in the chiral space group $P3_2$ forming conglomerates having either M or P helices. The catemers of order 2 do not show the same behavior. **3** crystallizes in the chiral space group $P2_1\,2_1\,2_1$ whereas **4** crystallizes as a less common racemic mixture in the space group $P2_1/n$ where the two helices (enantiomers) are present in the unit cell (Figure 1).[5b]

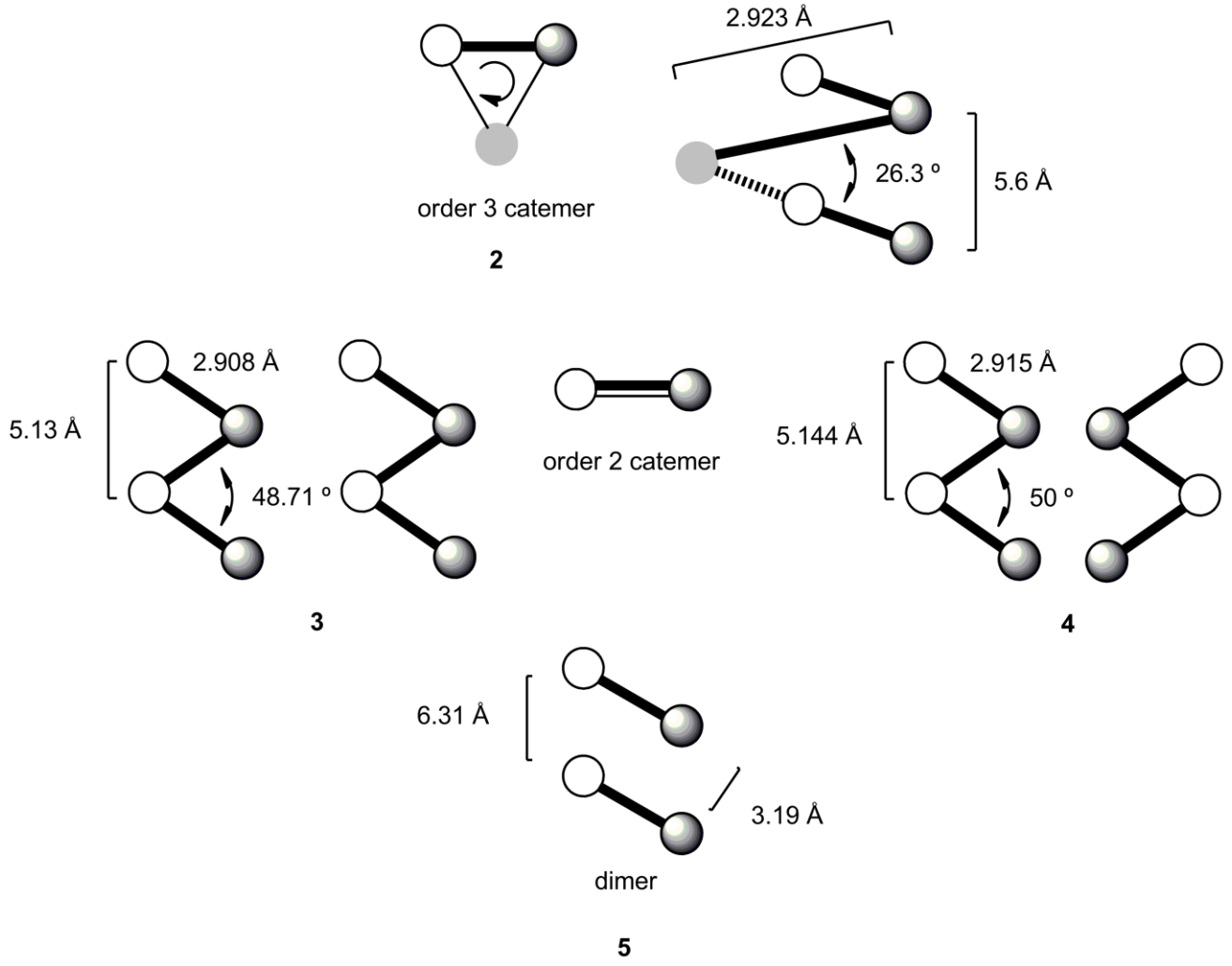


Figure 1. Schematic representation of the supramolecular structures of indazoles **2-5**

Table 4 summarizes distances and angles for the NH…N' hydrogen-bonding motifs that are common to the supramolecular structures of **2-5**. The hydrogen bonds have similar values for the indazoles **2-4** forming catemers (2.06-2.09 Å). **5** that forms dimers exhibits the shortest N(1)…N(2)' but also the longest hydrogen bond (more than 0.14 Å) and the smallest NH…N' angle. Table 5 summarizes parameters describing aromatic interactions in the catemers **2-4** with a comparison with **1**. We tentatively suggest that the variation of supramolecular structures from catemers of order 3 then 2 and then to dimer as the length of the perfluoroalkyl chain increases is mainly due to increasing steric interactions (as proposed for 1*H*-pyrazoles)[17] that cannot be counterbalanced by aromatic and related attractive interactions. Only dimers have been observed for several 3-aryl substituted 1*H*-tetrafluoroindazoles.[10c]

The 3-C_2F_5 substituted indazole **2** (Figure 1 and 2) crystallizes as a catemer of order 3 extending along the crystallographic axis *c*, just like the 3-CF_3 indazole **1**. As seen from Table 5, the main difference with **1** is a weaker aromatic interaction[18] between equivalent molecules along the chain as can be traced from longer *c* and larger distances between like centroids and larger offsets. The angles between each indazole along the chain are 73° and 86° in **1** and **2**, respectively. There are close contacts that are less than the sum of van de Waals radii between fluorines (2.94 Å)[19] and between fluorines and aromatic carbons (3.09(1), 3.14(1) Å, CF...Π interactions) along the chains.[1d,e,18] There is short distance (2.75(1) Å) between F12 (C9-F12 from the CF_3 group) and F7 (benzo C7-F7) of consecutive molecules. One fluorine of the CF_2 group shows close contacts with C8F8…C5 (3.14(1) Å) and C8F8…C6 (3.09(1) Å) (F8…Ctd 2.90(1); F8…plane 2.89(1) Å) where C5 and C6 are benzo carbons of the equivalent indazole along the chain. These contacts at best very weakly attractive[1d,e,18] and most probably are the result of the packing which is dictated by the NH…N and aromatic interactions. There are similar types of contacts (2.76(1) – 2.92(1) Å range) between fluorines of adjacent chains.

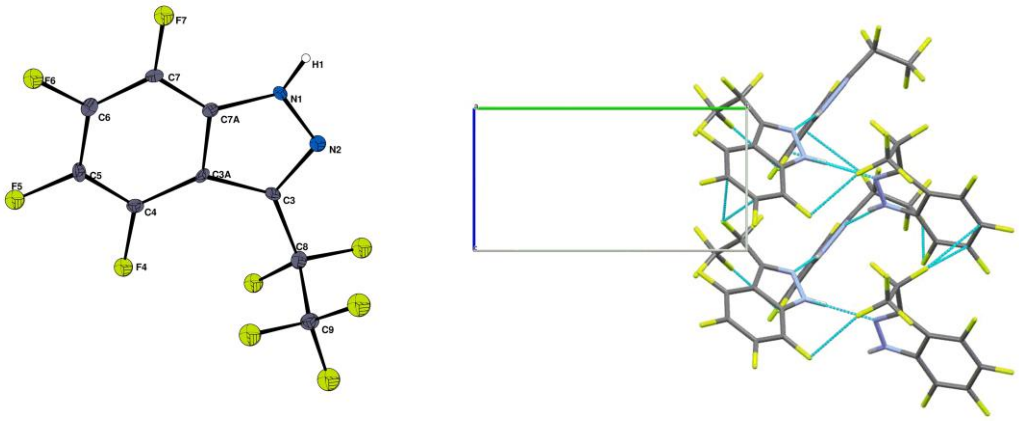


Figure 2. Molecular and supramolecular structure of **2** with the main short contacts highlighted. Ellipsoids are drawn at the 30% probability level.

The 3-C_3F_7 and 3-C_4F_9 substituted indazoles **3** (Figure 3) and **4** (Figure 4), respectively, both crystallize as catemers of order 2. The main difference is that **3** exhibit only one type of helix whereas the two enantiomers are present for **4** (see above and Figure 1). Actually, the metrical parameters defining the network of hydrogen bonding and the aromatic interactions are almost identical (Table 5). They are also more similar to those for **1** than those for **2** suggesting that the structure of **2** can be considered as an end point for a catemer of order 3. Within a chain, similar short contacts between a fluorine of the α-CF_2 and benzo carbons are present in both **3** [C8-F9…C3a 3.11(1) Å (118(1)°)] and **4** [C8-F8…C3a 3.11(1) Å (123(1)°); C8-F8…C7a 3.13(1) Å (103(1)°)]. In **4**, there are also short F…F contacts between β- and γ-CF_2 along the chain [C10-F13…F10-C9 2.91(1) Å (137(1), 113(1)°)].

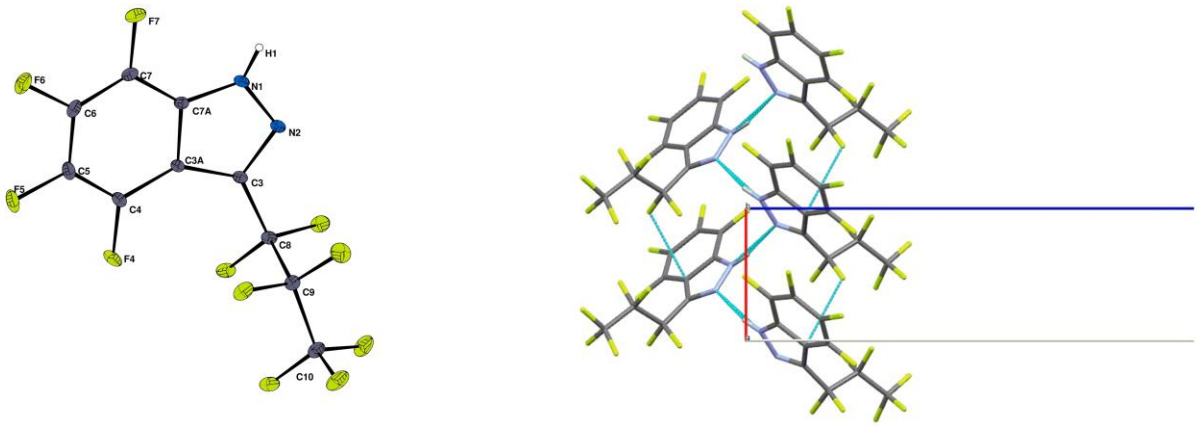


Figure 3. Molecular and supramolecular structure of **3**. Ellipsoids are drawn at the 30% probability level.

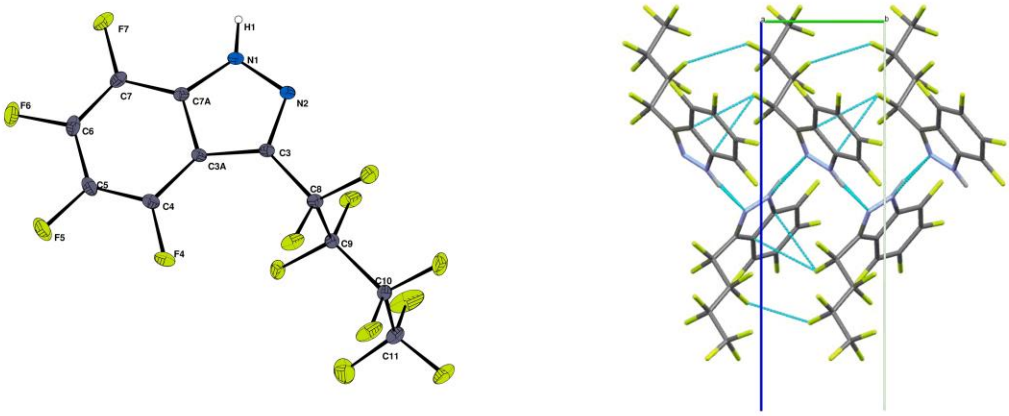


Figure 4. Molecular and supramolecular structure of **4** with the main short contacts highlighted. Ellipsoids are drawn at the 30% probability level.

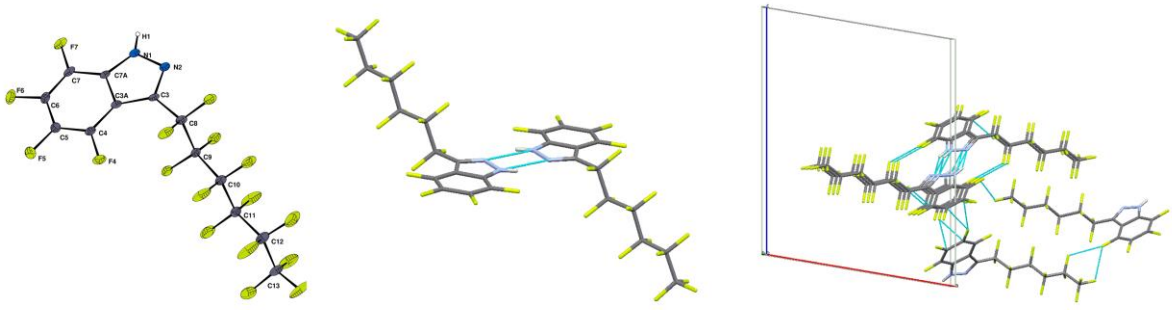


Figure 5. Molecular and supramolecular structure of **5** with the main short contacts highlighted. Ellipsoids are drawn at the 30% probability level.

Indazole **5** (Figure 5) crystallizes (monoclinic, *P* 2_1/c) as hydrogen bonded dimers that stack along the *b* axis. The two units of the dimer are related by an inversion center in which the aromatic parts are coplanar. The perfluorohexyl ponytail extends approximately in a plane that makes an angle of 80° with the plane of the indazole. There is a slight, nearly helicoidal, twist along the chain with C-C-C-C torsion angles averaging 176°. The repeating planes of the dimers are 3.19 Å apart and the angle with direction *b* is 60° (Figure 1 and 5). The benzo centroids are separated by *b* (6.308(2) Å) along the stacks (offset 5.44 Å) leading to an overall attractive stacking in which the pyrazolyl part contributes as well. Close contacts shorter than the sum of van der Walls radii can be noticed within a stack as C8-F8…C4 (3.09(1) Å, 126(1)°) and C7-F7…F10 (2.91(1) Å, 144(1)°) involving α-F and β-F fluorines on the saturated chain and carbon and fluorine on the aromatic benzo ring, respectively. There are close contacts with neighboring chains of the C-F…aromatic type [C5-F5…C6 3.14(1) Å (158(1)°), C5-F5…C5 3.17(1) Å (135(1)°)] and also between remote aliphatic fluorines F17 and F20 and aromatic fluorines F4 and F7 [C4-F4…F17 2.87(1) Å (157(1)°), C4-F4…F20 2.86(1) Å (128(1)°), C7-F7…F20-C13 2.90(1) Å (97(1), 93(1)°)]. In the absence of an in-depth study that is out of the scope of this paper, we suggest these close contacts are at best individually weak but that they contribute together with other forces to a given packing.[1d,e,18] Actually, similar parameters are observed in the structures of all the indazoles **2-5** and we suggest the increase of steric constraints imposed by the increasing length of the perfluoroalkyl chain becomes competitive and counterbalances other types of interactions. [1d,e,18,20]

Hydrotris(indazolyl)borates. We have been able to get the X-ray crystal structure of compound **7** (Table 3) that with a 3-heptafluoropropyl chain (Figure 6). The structure is a distorted trigonal pyramidal coordination for thallium with one Tl-N bond (Tl1-N3) slightly longer than the other two. The average of the Tl-N distances (2.69 Å) is longer than the average for TlTp' (2.59 Å) and for Tl((F_{21}-$Tp^{4Bo,3CF3}$) (2.61 Å).[10a] The N-Tl-N angles are all very close to the average of 71.1°, more acute than the average for TlTp' (75.1°). The Tl-N distances (resp. angles) are also longer (resp. more acute) than for another 3-heptafluoropropyl scorpionate[3h] $TlTp^{C3F7,Me}$ suggesting an even weaker interaction between Tl and the fluorinated ligand. Even in the absence of a symmetry element, the three $CF_2CF_2CF_3$ chains adopts a

propeller helicoidal conformation not dissimilar to that in $TlTp^{C3F7,Me}$ (symmetry imposed). As a result the Tl is almost completely buried in a nest of C-F bonds from the α-CF_2 and β-CF_2. The remarkable consequence is that among eight F from the α- and β-difluoromethylene groups pointing at Tl, there are seven close intramolecular Tl…F contacts in the range 3.061(6) – 3.413(7) Å (sum of the Van der Waals radii of Tl and F, 3.43 Å),[19] with the eighth being 3.486(7) Å. As a consequence of this shielding, there are no *intermolecular* contacts involving Tl. Ignoring the co-crystallized half molecule of CH_2Cl_2, short contacts between one CF_2-F and a Cbenzo-F (3.15(1) Å) and between a C-Fbenzo…CCbenzo (2.98(1) and 3.14(1) Å) can be noticed between two molecules related by the inversion center.

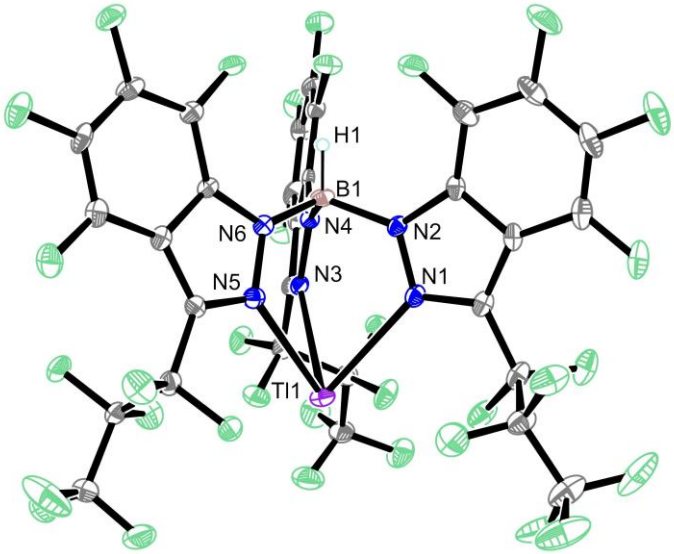


Figure 6. Molecular structure of $Tl[F_{33}\text{-}Tp^{4Bo,3C3F7}]$ (**7**). Ellipsoids are drawn at the 30% probability level. Relevant Bond Lengths (Å) and Angles (deg): N(1)-Tl(1) 2.671(6), N(3)-Tl(1) 2.709(5), N(5)-Tl(1) 2.683(6), N(2)-B(1) 1.580(10), N(4)-B(1) 1.543(9), N(6)-B(1) 1.520(11); N(1)-Tl(1)-N(5) 71.48(18), N(1)-Tl(1)-N(3) 70.72(16), N(5)-Tl(1)-N(3) 71.10(17).

Conclusion

New highly perfluorinated hydrotris(3-perfluoroalkylindazol-1-yl)borates have been synthesized by a new methodology. The sodium and thallium complexes have been fully characterized as well as the new indazoles. The single crystal X-ray structures for all indazoles show a variation in the supramolecular organization that depends on the perfluoroalkyl chain length. The study of their coordination properties with different transition metals and the catalytic activities for C-H bond activation of these complexes have already shown their potential as ligands. We are looking forward new applications of these strongly electron withdrawing perfluorinated molecules and anions.

Experimental Section

All syntheses requiring inert atmosphere were carried out using Schlenck or glovebox techniques. The solvents were dried and distilled using the conventional methods: diethyl ether and tetrahydrofuran (Na/benzophenone), toluene (Na), dichloromethane, pentane and dimethoxyethane (calcium hydride). Triethylsilane was dried and distilled under calcium hydride. Methyl pentafluoropropionate, methyl pentafluorobutyrate, methyl perfluorobenzoate, perfluorohexyl iodide, perfluorobutyl iodide were used as purchased. NMR experiments were acquired at 298 K using ARX250, DPX300, AV300 and AV400 Bruker spectrometers. ^{19}F NMR data for indazoles **2-5** and for hydrotris(indazolyl)borates **7-10** and collected in Table 1 and 2 respectively. Elemental Analysis were performed in the Analytic Services of our Laboratory. Mass Spectrometry measurements were recorded on a QTRAP Applied Biosystems Mass Spectrometer.

Synthesis of 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1-*H*-indazole (2)

Synthesis of pentafluoroethylpentafluorophenylketone. Pentafluorobromobenzene (7.0 mL, 56.16 mmol) was dissolved in diethyl ether (20 mL) and cooled at -80ºC. n-Butyllithium (22.5 mL of 2.5 M solution in hexanes, 56.25 mmol) was added dropwise over a period of 30 min. The mixture was stirred for another 10 min at low temperature. Then, a solution of methyl pentafluoropropionate (7.20 mL, 56.32 mmol) in diethyl ether (15 mL) was added in once and the reaction was stirred during 5 min before being quenched with HCl at 0°C (2N, 133 mL). The mixture was stirred during 1 hour to reach room temperature. The two phases were separated and the aqueous phase was extracted three times with

diethyl ether (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were removed under vacuum at 0ºC to yield a colorless liquid. This product was used without further purification in the next step of the synthesis.

Synthesis of 3-pentafluoroethyl-4,5,6,7-tetrafluoro-1-*H*-indazole (2). The perfluorinated ketone was dissolved in toluene (70 mL) and the mixture was cooled down to 0ºC. Hydrazine monohydrate (2.73 mL, 56.28 mmol) was then added dropwise and the mixture was stirred for another 1h at low temperature. The reaction mixture was then heated to reflux overnight yielding a yellow mixture with a brown aqueous phase. The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were evaporated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/hexane 1:1). The product was then sublimed at 70ºC under vacuum to afford white needles (11.78 g, 38.2 mmol, 68%). Anal. Calcd. (%) for $C_9HF_9N_2$ C 35.08, H 0.33, N 9.09. Found: C, 35.06; H, 0.0; N, 9.43.

Synthesis of 3-heptafluoropropyl-4,5,6,7-tetrafluoro-1-*H*-indazole (3).

Synthesis of heptafluoropropylpentafluorophenylketone. Pentafluorobromobenzene (2.7 mL, 22.0 mmol) was dissolved in diethyl ether (50 mL) and cooled at -80ºC. n-Butyllithium (8.8 mL of 2.5 M solution in hexanes, 22.0 mmol) was added dropwise over a period of 30 min. The mixture was stirred for another 15 min at low temperature. A solution of methyl heptafluorobutyrate (3.4 mL, 22.0 mmol) in diethyl ether (10 mL) was added at once and the reaction was stirred during 5 min before being quenched with HCl at 0°C (2N, 53 mL). The mixture was stirred during 1 hour to reach room temperature. The two phases were separated and the aqueous phase was extracted with diethyl ether (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were removed under vacuum at 0ºC to yield a colorless liquid. This product was used without further purification in the next step of the synthesis.

Synthesis of 3-heptafluoropropyl-4,5,6,7-tetrafluoro-1*H*-indazole (3). The perfluorinated ketone was dissolved in toluene (50 mL) and cooled down to 0ºC. Hydrazine monohydrate (0.96 mL, 22.0 mmol) was added dropwise and the mixture was stirred for another 1h at low temperature. The reaction

mixture was heated to reflux overnight yielding a yellow mixture with a brown aqueous phase. The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles were evaporated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/hexane 1:2). The product was then sublimed at 70ºC under vacuum to afford white needles (5.67 g, 15.9 mmol, 72%). $^{13}C\{^1H\}$ NMR (75.47 MHz, acetone-d_6): δ 139.8 (dptd, J = 238, 16, 2 Hz, C-5), 137.8 (ddpt, J = 253, 13, 4 Hz, C-4), 136.8 (dpt, J = 246, 16 Hz, C-6), 132.9 (dddd, J = 236, 5, 3 Hz, C-7), 132.8 (m, C-3), 131.4 (ddd, J = 14, 8, 4 Hz, C-7a), 117.9 (qt, J = 287, 36 Hz, *CF₃*), 112.7 (ptpt, J = 254, 32 Hz, *CF₂*-CF_2), 108.9 (ptq, J = 265, 38 Hz, *CF₂*-CF_3) 107.9 (dd, J = 20, 2 Hz, C-3a). Anal. Calcd. (%) for $C_{10}HF_{11}N_2$: C, 33.54; H, 0.28; F, 58.36; N, 7.82 Found: C, 33.56; H, 0.07; F, 58.36; N, 8.29.

Synthesis of 3-nonafluorobutyl-4,5,6,7-tetrafluoro-1*H*-indazole (4)

Synthesis of nonafluorobutylpentafluorophenylketone. Methyl pentafluorobenzoate (3 g, 13.3 mmol) and a solution of nonafluorobutyl iodide (10 mL, 58.1 mmol) in diethyl ether (110 mL) were introduced in a 250 mL Schlenk flask equipped with a dropping funnel. This solution was cooled down to -110°C and methyllithium lithium bromide complex (37 mL of 1.5 M solution in diethyl ether, 55.9 mmol) was added dropwise during 1 hour. The reaction was left to stir at -110°C during 45 minutes and then a solution of HCl 2N (150 mL) was added. Once at room temperature, the organic phase was separated and the aqueous phase was extracted with diethyl ether (2 x 25 mL). The solvent was evaporated under vacuum at 0°C. The residue was purified by silica-gel column chromatography (CH_2Cl_2/hexane, 1:5) and the volatiles were removed under vacuum to afford a colorless oil (4.5 g, 83 % yield) that was used without further purification in the next step of the synthesis.

Synthesis of 3-nonafluorobutyl-4,5,6,7-tetrafluoro-1*H*-indazole (4). The ketone (3.17 g, 7.66 mmol) was dissolved in toluene (40 mL) and the solution was cooled to 0°C. Hydrazine (0.645 mL, 13.3 mmol) was then added dropwise and the mixture was stirred at 0°C for 1h. The mixture was then heated up to 110°C and stirred under reflux overnight. The toluene phase was separated and the aqueous phase was extracted with diethyl ether (3 x 5 mL). All the organic phases were mixed and dried over $MgSO_4$.

After filtration and evaporation of the solvent, the indazole was purified by silica-gel column chromatography (CH_2Cl_2/hexane, 1:1) to give a white powder after evaporation of the volatiles. The product was then sublimed at 70ºC under vacuum to afford white needles (1.16 g, 2.84 mmol, 37 % yield). Anal. Calcd. (%) for $C_{11}HF_{13}N_2$ C 32.37, H 0.25, N 6.86. Found: C 32.29, H 0.0, N 7.03.

Synthesis of 3-tridecafluorohexyl-4,5,6,7-tetrafluoro-1*H*-indazole (5)

Synthesis of tridecafluorohexylpentafluoroketone. Following a similar procedure as that for nonafluorobutylpentafluorophenylketone, methyl pentafluorobenzoate (5 g, 22.1 mmol) and tridecafluorohexyl iodide (21.0 mL, 97.3 mmol) yielded a colorless oil (11.2 g, 98% yield) that was used without further purification in the next step of the synthesis.

Synthesis of 3-tridecafluorohexyl-4,5,6,7-tetrafluoro-1*H*-indazole (5). Hydrazine (1.29 mL, 26.5 mmol) was added dropwise to a solution of the ketone (11.2 g, 21.8 mmol) in toluene (100 mL) and the mixture was stirred at RT for 1h. The mixture was then heated up to 110°C and stirred under reflux overnight. The toluene phase was separated and the aqueous phase was extracted with diethyl ether (3x10 mL). All the organic phases were mixed and dried over $MgSO_4$. After filtration and evaporation of solvent, the indazole was purified by silica-gel column chromatography (CH_2Cl_2/hexane, 1:1) to give a white powder after evaporation of the volatiles. The product was then sublimed at 90ºC under vacuum to afford white needles (7.2 g, 14.2 mmol, 65% yield). Anal. Calcd. (%) for $C_{13}HF_{17}N_2$ C 30.73, H 0.20, N 5.51. Found: C 30.63, H 0.0, N 5.75.

Synthesis of sodium hydrotris(3-pentafluoroethyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Na[F_{27}-$Tp^{4Bo,3CF2CF3}$]

A solution of **2** (500 mg, 1.62 mmol) in DME (5 mL) was added dropwise to a suspension of NaH (38 mg, 1.57 mmol) in DME (5 mL) at 0°C. The resulting yellow solution was stirred for 1 hour at room temperature. In a 20 mL Schlenk flask, boron tribromide (50 µL, 0.51 mmol) was cooled down to -40°C. $HSiEt_3$ (81 µL, 0.51 mmol), previously distilled over CaH_2, was then added and the mixture was stirred at -40°C for 10 minutes to generate $HBBr_2$ *in situ*. The solution of the sodium indazolate was added to the $HBBr_2$ mixture at -40°C and the resulting mixture was stirred during 30 minutes at that temperature

before being refluxed at 85°C for 3 days. The mixture was then cooled to room temperature, filtered over celite and the solvent was evaporated to dryness. The residue was solubilized in toluene and the product was obtained by precipitation with hexane. The solid was washed with hexane (3 x 10 mL) and dried under vacuum to yield a white powder (229 mg, 0.24 mmol, 47% yield). ESI-MS m/z (relative intensity): 933.2 (100, M^-).

Synthesis of thallium hydrotris(3-pentafluoroethyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Tl[F_{27}-Tp ^{4Bo,3CF2CF3}] (6).

A solution of Tl_2SO_4 (244 mg, 0.48 mmol) in water (35 mL) was added to a solution of Na[F_{27}-$Tp^{4Bo,3CF2CF3}$] (842 mg, 0.88 mmol) in chloroform (50 mL). The mixture was stirred overnight at room temperature. The organic phase was separated and the aqueous phase was extracted with chloroform (2 x 10 mL). The combined organic phase was dried with Na_2SO_4, the solution was filtered and the solvent was evaporated under vacuum to afford a white solid. The solid was washed with dichloromethane, pentane and dried under vacuum (738 mg, 0.65 mmol, 74% yield). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3OD): δ 139.1 (dptd, J = 247, 16, 2 Hz, C-5), 137.2 (ddpt, J = 247, 12, 4 Hz, C-4), 135.5 (dpt, J = 244, 16 Hz, C-6), 134.4 (dddd, J = 252, 13, 5, 2 Hz, C-7), 131.7 (m, C-7a), 131.4 (m, C-3) 118.9 (qt, J = 285, 37 Hz, CF_3), 111.2 (ptd, J = 249, 39 Hz, CF_2), 109.1 (dd, J = 19, 4 Hz, C-3a). $^{11}B\{^1H\}$ NMR (96.29 MHz , acetone-d_6): δ 0.03 (br s, BH). ^{11}B NMR (96.29 MHz, acetone-d_6): δ 0.03 (br q, J = 107 Hz, BH). Anal. Calcd. (%) for $C_{27}HBF_{27}N_6Tl$: C 28.51, H 0.09, N 7.39. Found: C 28.39, H 0.00, N 7.37.

Synthesis of sodium hydrotris(3-heptafluoropropyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Na[F_{33}-$Tp^{4Bo,3CF2CF2CF3}$]

Following a similar procedure as that for Na[F_{27}-$Tp^{4Bo,3CF2CF3}$], **3** (1 g, 2.79 mmol), boron tribromide (82 µL, 0.87 mmol) and $HSiEt_3$ (139 µL, 0.87 mmol) with a longer refluxing time (5 days), yielded Na[F_{33}-$Tp^{4Bo,3CF2CF2CF3}$] as a white powder after work-up (690 mg, 0.62 mmol, 71% yield). Anal. Calcd. (%) for $C_{30}HBF_{33}N_6Na$: C 32.57, H 0.09, N 7.60. Found: C 31.96, H 0.00, N 7.47. ESI-MS m/z (relative intensity): 1083.1 (100, M^-).

Synthesis of thallium hydrotris(3-heptafluoropropyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Tl[F_{33}-$Tp^{4Bo,3CF2CF2CF3}$] (7)

A solution of Tl_2SO_4 (244 mg, 0.48 mmol) in water (35 mL) was added to a solution of Na[F_{33}-$Tp^{4Bo,3CF2CF2CF3}$] (842 mg, 0.88 mmol) in chloroform (50 mL). The mixture was stirred overnight at room temperature. The organic phase was separated and the water phase was extracted with chloroform (or Et_2O) (2 x 10 mL). The combined organic phase was dried with Na_2SO_4 (or $MgSO_4$), the solution was filtered and the solvent was evaporated under vacuum to afford a white solid. The solid was washed with dichloromethane, pentane and dried under vacuum (840 mg, 0.65 mmol, 74% yield). $^{13}C\{^1H\}$ NMR (75.47 MHz, acetone-d_6): δ 139.2 (dptd, J = 247, 15, 2 Hz, C-5), 137.08 (ddpt, J = 25, 12.2, 4 Hz, C-4), 135.7 (dpt, J = 244, 15.8, C-6), 134.6 (dddd, J = 252, 134, 5, 3 Hz, C-7), 131.7 (m, C-3), 131.4 (m, C-7a), 117.9 (qt, J = 287, 34 Hz, CF_3), 112.9 (ptpt, J = 252, 31 Hz, CF_2), 109.5 (dd, J = 18, 4 Hz, C-3a), 108.9 (ptq, J = 265, 37 Hz, CF_2). $^{11}B\{^1H\}$ NMR (96.29 MHz , acetone-d_6): δ -0.80 (broad, BH). Anal. Calcd. (%) for $C_{30}HBF_{33}N_6Tl$: C 27.98, H 0.08, N 6.52. Found: C 26.79, H 0.00, N 6.31. ESI-MS m/z (relative intensity): (100, M^-) 1083.1, (100, M^+) 204.8.

Synthesis of sodium hydrotris(3-nonafluorobutyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Na[F_{39}-$Tp^{4Bo,3CF2CF2CF2CF3}$]

Following a similar procedure as that for Na[F_{27}-$Tp^{4Bo,3CF2CF3}$], **4** (1.63 g, 3.99 mmol), boron tribromide (120 µL, 1.25 mmol) and $HSiEt_3$ (200 µL, 1.25 mmol) with a longer refluxing time (5 days), yielded Na[F_{33}-$Tp^{4Bo,3CF2CF2CF2CF3}$] as a white powder after work-up (980 mg, 0.78 mmol, 62% yield).

Synthesis of thallium hydrotris(3-nonafluorobutyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Tl[F_{39}-$Tp^{4Bo,3CF2CF2CF2CF3}$] (8)

A solution of Tl_2SO_4 (217 mg, 0.43 mmol) in water (30 mL) was added to a solution of Na[F_{39}-$Tp^{4Bo,3CF2CF2CF2CF3}$] (980 mg, 0.78 mmol) in chloroform (45 mL). The mixture was stirred overnight at room temperature. The organic phase was separated and the water phase was extracted with chloroform (or Et_2O) (2 x 10 mL). The organic phase was dried with Na_2SO_4 (or $MgSO_4$), the solution was filtered and the solvent was evaporated under vacuum to afford a white solid. The solid was washed with

dichloromethane, pentane and dried under vacuum (950 mg, 0.66 mmol, 85% yield). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, acetone-d^6): δ 139.0 (dptd, J = 245, 16, 2 Hz, C-5), 137.2 (ddpt, J = 251, 12, 4 Hz, C-4), 135.7 (dpt, J = 243, 16 Hz, C-6), 134.5 (dddd, J = 254, 13, 5, 3 Hz, C-7), 131.9 (m, C-3), 131.5 (m, C-7a), 117.5 (qt, J = 288, 33 Hz, CF_3), 113.4 (ptpt, J = 253, 31 Hz, CF_2-C=N), 110.6 (ptpt, J = 254, 31 Hz, $CF_2CF_2CF_2$), 109.5 (dd, J = 178, 34 Hz, C-3a), 108.8 (ptq, J = 268, 38 Hz, CF_3CF_2). ^{11}B NMR (96.29 MHz, acetone-d^6): δ -0.68 (broad, BH). Anal. Calcd. (%) for $C_{33}HBF_{39}N_6Tl$: C 27.57, H 0.07, N 5.85. Found: C, 27.15, H 0.00, N 6.03. ESI-MS m/z (relative intensity): (100, M^-) 1233.4, (100, M^+) 204.8.

Synthesis of sodium hydrotris(3-tridecafluorohexyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Na[F_{51}-Tp $^{4Bo,3(CF2)5CF3}$]

Following a similar procedure as that for Na[F_{27}-Tp^{4Bo,3CF2CF3}], **5** (2.62 g, 5.16 mmol), boron tribromide (152 µL, 1.61 mmol) and (257 µL, 1.61 mmol) with a longer refluxing time (5 days), yielded Na[F_{33}-Tp^{4Bo,3CF2CF2CF2CF3}] as a white powder after work-up (1.57 g, 63% yield)..

Synthesis of thallium hydrotris(3-perfluorohexyl-4,5,6,7-tetrafluoroindazol-1-yl)borate, Tl[F_{51}-Tp $^{4Bo,3CF2(CF2)4CF3}$] (9)

A solution of Tl_2SO_4 (280 mg, 0.55 mmol) in water (40 mL) was added to a solution of Na[F_{51}Tp] (1.57 g, 1.00 mmol) in chloroform (60 mL). The mixture was stirred overnight at room temperature. The organic phase was separated and the water phase was extracted with chloroform (or Et_2O) (2 x 10 mL). The organic phase was dried with Na_2SO_4 (or $MgSO_4$), the solution was filtered and the solvent was evaporated under vacuum to afford a White solid. The product was washed with dichloromethane and pentane and the product was dried under vaccum (960 mg, 0.55 mmol, 55% yield). ^{11}B NMR (96.29 MHz, acetone-d_6): δ 0.33 (broad, BH). Anal. Calcd. (%) for $C_{39}HBF_{51}N_6Tl$: C 26.96, H 0.06, N 4.84. Found: C 26.15, H 0.00, N 6.41. ESI-MS m/z (relative intensity): (100, M^-) 1533.2, (100, M^+) 204.8.

X-ray diffraction. The data were collected on a Bruker Kappa Apex II diffractometer (for **2**, **3** and **7**) equipped with an Oxford Cryosystems Cryostream cooler device or on an Agilent Technologies GEMINI EOS diffractometer (for **4** and **5**) equipped with an Oxford Instrument cooler device. Details of crystal data, data collection and refinement can be found in Table 3. The structures were solved by direct

methods using SIR92[21] or SHELX86[22] and refined by means of least-squares procedures on F^2 with the aid of the program SHELX-L97[22] included in the software package WinGX version 1.63.[23] All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were geometrically placed and refined by using a riding model. In the last cycles of refinement a weighting scheme was used, where weights were calculated from the following formula: $w = 1/[\sigma^2(Fo^2) + (0.0380P)^2 + 1.1258P]$ where $P = (Fo_2+2Fc^2)/3$. D to the small size of the crystal of **7**, diffraction intensity at high angles is incomplete causing an Alert A in the checkcif.[24]

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Electronic Supporting Information. CIF files for compounds **2 – 5** and **7**.

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24. CCDC 982666-982670 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax,(+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Table 1. ^{19}F NMR data (δ, ppm; *J*, Hz) of indazoles **2-5** in acetone-d_6.

	2	**3**	**4**	**5**
F4	-144.2 (m)	-143.8 (m)	-144.1 (m)	-143.9 (m)
F5	-164.7 (t)	-164.6 (td)	-164.6 (t)	164.8 (t)
	$^3J_{F6}$, $^3J_{F4}$ = 18.4	$^3J_{F6}$, $^3J_{F4}$ = 18.9	$^3J_{F6}$, $^3J_{F4}$ = 18.4	$^3J_{F6}$, $^3J_{F4}$ = 18.3
		$^4J_{F7}$ = 1.5		
F6	-157.9 (td)	-158.2 (td)	-158.1 (td)	-158.3 (td)
	$^3J_{F7}$, $^3J_{F5}$ = 18.3	$^3J_{F7}$, $^3J_{F5}$ = 18.9	$^3J_{F7}$, $^3J_{F5}$ = 18.3	$^3J_{F7}$, $^3J_{F5}$ = 18.1
	$^4J_{F4}$ = 1.7	$^4J_{F4}$ = 2.0	$^4J_{F4}$ = 2.0	$^4J_{F4}$ = 2.0
F7	-158.4 (t)	-158.8 (td)	-158.2 (td)	-158.6 (t)
	$^3J_{F6}$, $^5J_{F4}$ = 18.2	$^3J_{F6}$, $^5J_{F4}$ = 18.7	$^3J_{F6}$, $^5J_{F4}$ = 18.3	$^3J_{F6}$, $^5J_{F4}$ = 18.3
		$^4J_{F5}$ = 1.5	$^4J_{F5}$ = 1.5	
CF_2	-110.3 (dd)	Cα -108.9 (dqt)	Cα -108.3 (dtt)	Cα -108.3 (m)
	$^5J_{F4}$ = 23	$^5J_{F4}$ = 25	$^5J_{F4}$ = 24	Cβ,γ -122.3 (m)
	$^3J_{CF3}$ = 2	$^4J_{CF3}$ = 9.6	$^4J_{CF2}$ = 12	Cδ -123.5 (m)
		$^3J_{CF2}$ = 7.0	$^3J_{CF2}$ = 3	Cε -126.9 (m)
		Cβ -126.9 (dd,	Cβ -123.1 (m)	
		AA'BB' type)	Cγ -126.4 (m)	
		$^3J_{F-F}$ = 7, 17		
CF_3	-84.2 (t)	-81.2 (t)	-81.9 (tt)	-81.9 (t)
	$^3J_{CF2}$ = 2	$^4J_{CF2}$ = 9.6	$^4J_{CF2}$ = 9.9	$^4J_{CF2}$ = 10.2
			$^3J_{CF2}$ = 2.5	

Table 2. ^{19}F NMR data (δ, ppm; *J*, Hz) of hydrotris(indazolyl)borates **6-9** in acetone-d_6.

	6	**7**	**8**	**9**
F4	-145.7 (m)	-145.6 (m)	-145.5 (m)	-145.5 (m)
F5	-167.1 (t)	-167.1 (t)	-167.2 (t)	167.3 (t)
	$^3J_{F6} = {}^3J_{F4} = 19.1$	$^3J_{F6}, {}^3J_{F4} = 18.5$	$^3J_{F6}, {}^3J_{F4} = 18.9$	$^3J_{F6}, {}^3J_{F4} = 19.0$
F6	-155.3 (td)	-155.5 (td)	-155.6 (td)	-155.8 (td)
	$^3J_{F7} = {}^3J_{F5} = 18.3$	$^3J_{F7}, {}^3J_{F5} = 18.9$	$^3J_{F7}, {}^3J_{F5} = 18.3$	$^3J_{F7}, {}^3J_{F5} = 18.5$
	$^4J_{F4} = 8.7$	$^4J_{F4} = 9.2$	$^4J_{F4} = 9.5$	$^4J_{F4} = 9.4$
F7	-161.8 (t)	-162.7 (t)	-162.1 (t)	-162.1 (t)
	$^3J_{F6} = {}^5J_{F4} = 18.6$	$^3J_{F6}, {}^5J_{F4} = 19$	$^3J_{F6}, {}^5J_{F4} = 18.8$	$^3J_{F6}, {}^5J_{F4} = 18.9$
CF_2	-108.6 (d)	Cα -107.9 (br	Cα -106.9 (dt)	Cα -106.5 (dt)
	$^5J_{F4} = 23.4$	ddm)	$^5J_{F4} = 25$	$^5J_{F4} = 25$
		$^5J_{F4} = 25$	$^4J_{CF2} = 12$	$^4J_{CF2} = 12$
		$^4J_{CF3} = 9.0$	Cβ -123.6 (br s)	Cβ -121.9 (br s)
		Cβ -127.3 (br d)	Cγ -126.3 (br m)	Cγ -122.6 (br s)
		$J = 8.5$		Cδ -123.6 (br s)
				Cε -127.0 (br m)
CF_3	-84.0 (br s)	-81.2 (t)	-82.2 (t)	-81.9 (t)
		$^4J_{CF2} = 9.2$	$^4J_{CF2} = 10.0$	$^4J_{CF2} = 10.4$

Table 3. Crystal and Refinement data for **2-5** and **7**.

Parameters	**2**	**3**	**4**	**5**	**7**
Empirical Formula	$C_9HF_9N_2$	$C_{10}HF_{11}N_2$	$C_{11}HF_{13}N_2$	$C_{13}HF_{17}N_2$	$2(C_{30}HBF_{33}N_6Tl)$, CH_2Cl_2
Formula weight	308.12	358.13	408.13	508.16	2660.04
Temperature (K)	180(2)	180(2)	180(2)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	Hexagonal	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P3_2$	$P2_1\,2_1\,2_1$	$P2_1/n$	$P2_1/c$	P-1
Unit cell dimensions	*a*=12.4390(7)Å *b*=12.4390(7)Å *c*=5.5990(9) Å α = 90° β = 90° γ = 120°	*a*=5.1335(3) Å *b*=9.1624(5) Å *c*=24.8250(15)Å α = 90° β = 90° γ = 90°	*a*=9.3577(5) Å *b*=5.1436(2) Å *c*=27.2757(12)Å α = 90° β = 99.507 (5)° γ = 90°	*a*=14.1749(9) Å *b*=6.3085(5) Å *c*=18.2579(16)Å α = 90° β = 99.598(8)° γ = 90°	*a* = 12.7490(12) *b* = 13.0300(11) c = 14.4090(13) α = 97.161(4) β = 114.950(4) γ = 111.090(4)
Volume $Å^3$,Z	750.26 (13), 3	1167.65 (12), 4	1294.81(10), 4	1609.8(2), 4	1913.7(3), 1
density (Mg/m^3)	2.046	2.037	2.094	2.097	2.308
Abs. coefficient mm^{-1}	0.243	0.247	0.258	0.265	4.489
F(000)	450	696	792	984	1254
Crystal size (mm)	0.3x0.05x0.02	0.2x0.12x0.02	0.25x0.08x0.05	0.15x0.08x0.02	0.15 x 0.15 x 0.025
θ range for data collection	3.28 to 25.33°	3.32 to 33.04°	2.89 to 25.68°	3.38 to 26.37°	1.65 to 26.37
Limiting indices	-14≤h≤14, -14≤k≤14,	-7≤h≤7, -13≤k≤13,	-6≤h≤11, -6≤k≤6,	-17≤h≤17, -7≤k≤7,	-15≤h≤11, -16≤k≤16,

	-6≤l≤6	-36≤l≤37	-33≤l≤33	-22≤l≤22	-16≤l≤18
Reflns collected	7456	26389	8638	13951	28371
Reflns unique [R(int)]	912 [0.0139]	2432 [0.0338]	2457 [0.0223]	3287 [0.0584]	7287 [0.0465]
Completeness to θ	99.9% (25.33°)	95.3% (33.04°)	99.9% (25.68°)	99.8% (26.37°)	93.1% (26.37)
Data/restraints/params	912/2/124	2432/0/211	2457/1/238	3287/0/293	7287 / 0 / 658
Goodness of fit on F^2	1.092	1.098	1.073	0.864	1.172
Final R indices [I>2σ(I)]	R1 = 0.0637 wR2 = 0.1565	R1 = 0.0362 wR2 = 0.0907	R1 = 0.0416 wR2 = 0.1088	R1 = 0.0517 wR2 = 0.1237	R1 = 0.038 wR2 = 0.0876
R indices (all data)	R1 = 0.0649 wR2 = 0.1577	R1 = 0.0478 wR2 = 0.0978	R1 = 0.0508 wR2 = 0.1139	R1 = 0.1125 wR2 = 0.1395	R1 = 0.0668 wR2 = 0.1252
Largest residual peaks	0.604 and -0.584 e Å^{-3}	0.357 and -0.273 e Å^{-3}	0.671 and -0.427 e Å^{-3}	0.418 and -0.266 e Å^{-3}	0.887 and -1.458

Table 4. Selected bond distances (Å) and angles for the hydrogen bond network in **2-5**.

Bonds and angles	**2**	**3**	**4**	**5**
N(1)H(1)…N(2')	2.09(4)	2.09(3)	2.06(2)	2.21(3)
N(1)…N(2')	2.923(8)	2.908(2)	2.915(2)	2.876(4)
N(1)-H(1)-N(2')	165(7)	163(2)	160(2)	144(3)

Table 5. Metric parameters between equivalent parallel molecules in the catemers **1-4**

Distance/ Å	**1** [a]	**2**	**3**	**4**
Ctd – Ctd [b]	4.95	5.59(1)	5.13(1)	5.14(1)
Ctd – Ctd_pz [c]	6.30/4.31	6.94/4.89(1)	6.35/4.65(1)	6.29/4.75(1)
Ctd – plane	3.58	3.45(3)	3.41(1)	3.43(1)
Offset	3.42	4.41	3.84	3.83
Pitch	1.65	1.87	2.57	2.57

[a] from ref 8; [b] Ctd is benzo ring centroid; [c] Ctd_pz is pyrazolyl centroid

Table of content entry. Perfluorinated indazoles and hydrotris(indazolyl)borato complexes of thallium are synthesized and their molecular and supramolecular structures reveal various types of intra- and intermolecular interactions and organizations due to the high fluorine contents.