Chiral C_2 and C_1 symmetric (cyclooctane-1,5-diyl)bis(2-pyrazolyl)borate complexes of potassium and thallium. Preparation, structures and solution behavior

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The preparation, structures and solution behavior of {(cyclooctane-1,5-diyl)bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}metal, where metal = K, **1**, or Tl, **2**, {(cyclooctane-1,5-diyl)[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl][(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/3), **3**·3THF, and {(cyclooctane-1,5-diyl)bis[(4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/4), **4**·4THF, are reported.

Chiral bidentate phosphines and amines have found extensive use in catalysis and stoichiometric asymmetric organic transformations.[1] Similarly sterically demanding binolates, which are dianionic ligands, are finding increasing applications as chiral auxiliaries.[1b] We describe here a general route to chelating bidentate ligands which are uninegative and have pyrazole and indazole nitrogen donor atoms.

Results and discussion

Syntheses

The general method of synthesis is shown in reaction (1) (9-BBN = 9-borabicyclo[3.3.1]nonane).[2]

$$\text{(a)}\quad \text{pzH} + \text{KOH} \xrightarrow[\text{toluene}]{\text{reflux}} \text{Kpz} + \text{H}_2\text{O}$$

$$\text{(b)}\quad \text{9-BBN} + \text{pzH} + \text{Kpz} \xrightarrow[\text{toluene}]{\text{reflux}} \text{K((pz)}_2\text{BBN-9)} + \text{H}_2 \qquad (1)$$

The H_2O formed in reaction (1) was removed by using a Soxhlet apparatus containing finely divided CaH_2 through which the refluxing toluene was passed. The pyrazoles and indazoles employed in this work were those shown in Fig. 1. The potassium salts were obtained as air-stable, white crystalline products in the range of 70–85% theoretical yield based on reaction (1), except for the pulegone derived product which was obtained in *ca.* 20% yield. The syntheses of the chiral indazoles derived from (+)/(−)-camphor, (+)-menthone and (+)-pulegone are shown in Scheme 1.[3]

The single crystal and molecular structures were determined for the following four complexes: {(cyclooctane-1,5-diyl)bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}metal, where metal = K, **1**, or Tl, **2**; {(cyclooctane-1,5-diyl)[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl][(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/3), **3**·3THF, and {(cyclooctane-1,5-diyl)bis[(4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/4), **4**·4THF. In some instances these complexes were crystallized as THF solvates and their molecular structures are shown in Figs. 2 through 5. The formulae and selected bond distances and angles are given in Tables 1 and 2. A summary of crystallographic data is given in Table 3.

The features pertinent to these structures are as follows.

1. Despite certain crystallographic problems and poor structural refinements, there is no doubt about the general coordination geometry of the metal ions, nor the conformations of the ligands. The X-ray diffraction studies unambiguously show the absolute stereochemistry of the chiral carbon atoms.

2. Three of the structures, namely those of **1**, **2** and **4** have C_1 symmetry whereas that of **3**, which comprises both enantiomers of the camphor derived indazole, has a mirror plane of symmetry.

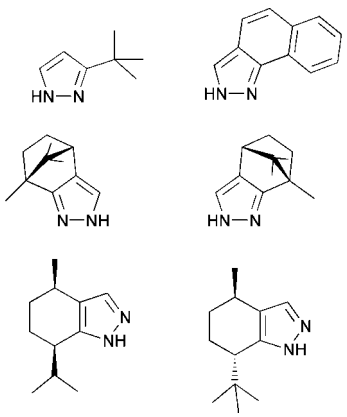
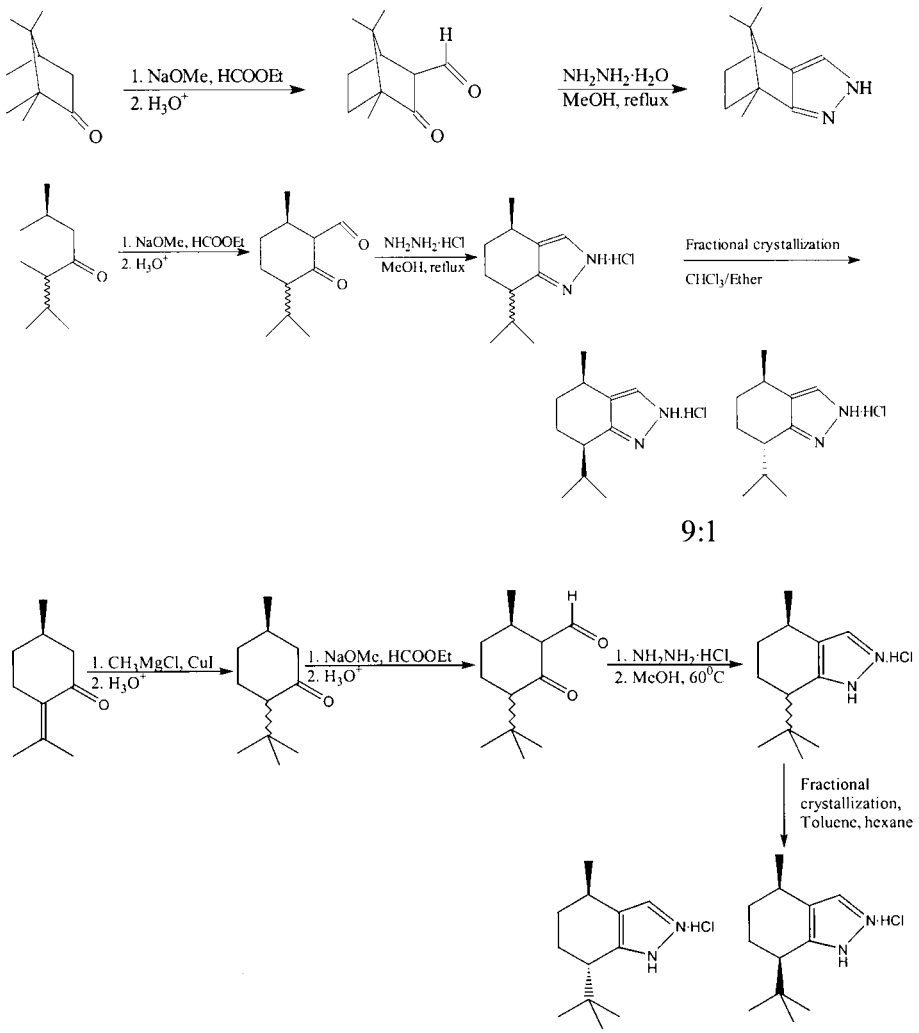
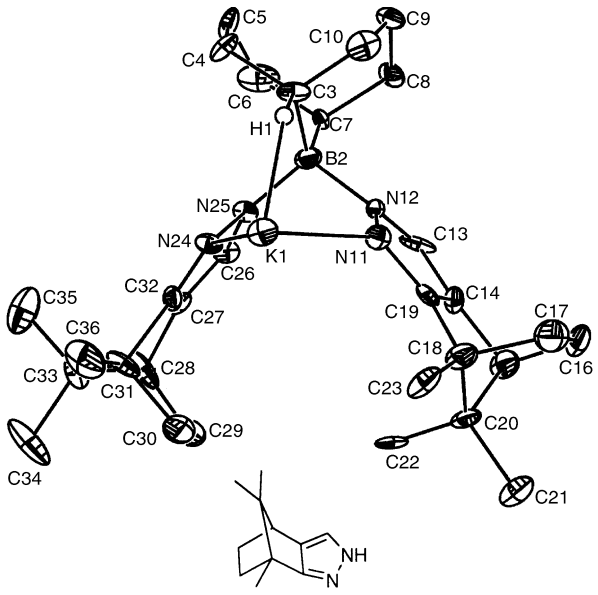


Fig. 1 The pyrazoles and indazoles employed in eqn. (1) are (clockwise, from top left) 3-*tert*-butylpyrazole, 2*H*-benz-4,5-dihydroindazol-2-yl, (4*R*,7*S*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-2-indazole, 7(*S*)-*tert*-butyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazole, 7(*R*)-isopropyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazole, (4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-2-indazole.

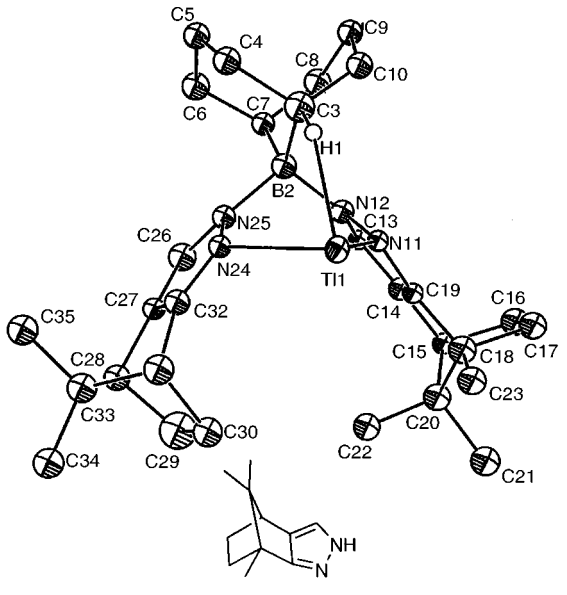


Scheme 1 The top reaction yields (4*R*,7*S*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-2-indazole and (4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-2-indazole. The middle reaction yields 7(*R*)-isopropyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazole and the bottom 7(*S*)-*tert*-butyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazole and 7(*R*)-*tert*-butyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazole.



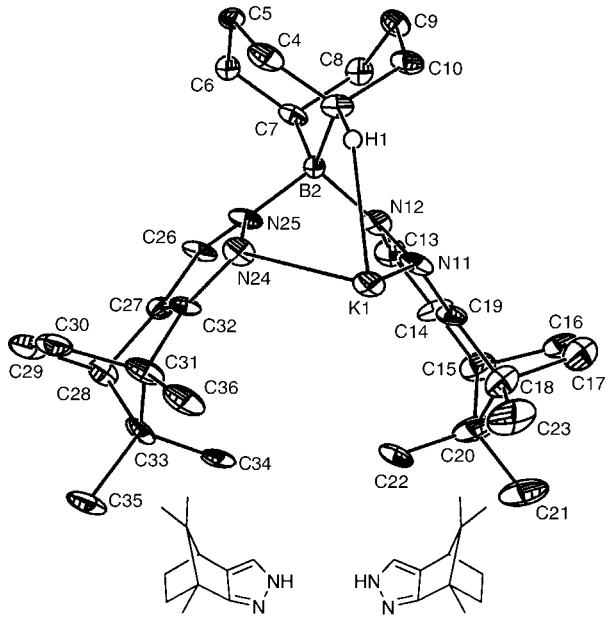
Ligand derived from (+)-camphor

Fig. 2 An ORTEP[10] diagram of {(cyclooctane-1,5-diyl)bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium, **1**, with the atom numbering scheme. The hydrogen atoms are omitted for clarity and the thermal ellipsoids are of 50% probability.



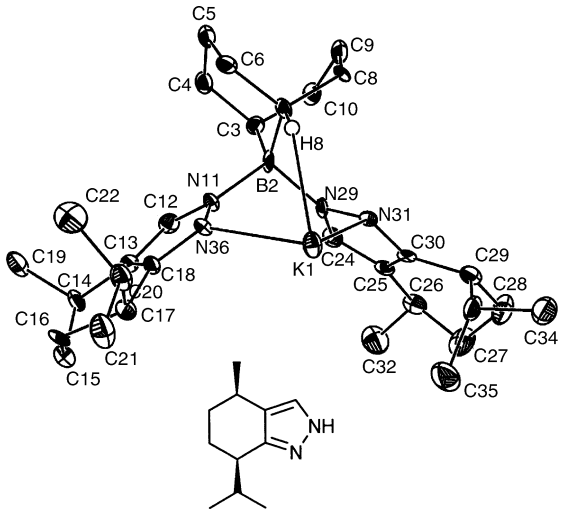
Ligand derived from (+)-camphor

Fig. 3 An ORTEP diagram of {(cyclooctane-1,5-diyl)bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}thallium, **2**, with the atom numbering scheme. The hydrogen atoms are omitted for clarity and the thermal ellipsoids are of 50% probability.



Ligands derived from (+)-and (-)-camphor

Fig. 4 An ORTEP diagram of {(cyclooctane-1,5-diyl)[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl][(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/3), **3**·3THF, with the atom numbering scheme. The hydrogen atoms and the THF molecules are omitted for clarity and the thermal ellipsoids are of 50% probability. The molecule, unlike **1**, **2** and **4**, has a mirror plane of symmetry.



Ligand derived from (+)-menthone

Fig. 5 An ORTEP diagram of {(cyclooctane-1,5-diyl)bis[(4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium–tetrahydrofuran(1/4), **4**·4THF, with the atom numbering scheme. The hydrogen atoms and the THF molecules are omitted for clarity and the thermal ellipsoids are of 30% probability.

Table 1 Selected bond distances (Å)

Compound **1**		Compound **4**	
K(1)–H(1)	2.673(1)	K(1)–H(8)	2.729(1)
K(1)–N(11)	2.750(7)	K(1)–N(31)	2.831(1)
K(1)–N(24)	2.797(7)	K(1)–N(36)	2.578(1)
Compound **2**		K(1)–O(37)	2.956(1)
T1(1)–H(1)	2.39(1)	K(1)–O(42)	2.722(1)
T1(1)–N(11)	2.47(1)	K(1)–O(47)	2.731(1)
T1(1)–N(24)	2.56(1)	K(1)–O(52)	2.810(1)
Compound **3**			
K(1)–H(1)	2.923(1)		
K(1)–N(24)	2.741(1)		
K(1)–N(11)	2.779(1)		

Table 2 Selected bond angles (°)

Compound **1**		Compound **2**	
N(11)–K(1)–N(24)	68.5(2)	N(11)–Tl(1)–N(24)	78.2(5)
N(11)–K(1)–H(1)	60.9(1)	N(12)–B(2)–N(25)	104.7(2)
N(24)–K(1)–H(1)	62.8(1)	N(12)–B(2)–C(7)	112.6(2)
N(12)–B(2)–N(25)	103.5(5)	N(12)–B(2)–C(3)	113.6(2)
N(12)–B(2)–C(7)	114.2(7)	N(25)–B(2)–C(7)	112.0(2)
N(25)–B(2)–C(3)	113.6(7)	N(25)–B(2)–C(3)	110.4(2)
N(25)–B(2)–C(7)	110.1(7)	C(7)–B(2)–C(3)	103.7(2)
C(3)–B(2)–C(7)	105.6(5)		
Compound **3**		Compound **4**	
N(11)–K(1)–N(24)	73.18(1)	H(8)–K(1)–N(36)	61.4(2)
N(24)–K(1)–H(1)	60.99(1)	H(38)–K(1)–N(31)	61.0(1)
N(11)–K(1)–H(1)	62.30(1)	N(36)–K(1)–N(31)	82.4(1)
N(12)–B(2)–N(25)	104.68(3)	O(42)–K(1)–O(47)	84.1(1)
N(12)–B(2)–C(3)	114.05(3)	O(42)–K(1)–O(52)	78.5(1)
N(12)–B(2)–C(7)	111.44(2)	N(11)–B(2)–N(23)	105.6(4)
N(25)–B(2)–C(3)	111.88(3)	N(11)–B(2)–C(3)	110.5(4)
N(25)–B(2)–C(7)	110.65(2)	N(11)–B(2)–C(7)	112.4(4)
C(3)–B(2)–C(7)	104.28(3)	N(23)–B(2)–C(7)	113.0(4)
		C(3)–B(2)–C(7)	105.0(4)

3. The $B(NN)_2M$ ring in all four structures has a bent twist-boat like structure with the boron atom clearly out of the plane and displaced toward the metal, see Fig. 6. This brings the bridgehead hydrogen in close proximity to the metal ions. The average N–N–B angle is 120° and the average C–H···M distance (the C–*H* atoms were located in each of the four structures) is 2.7 and 2.4 Å for the K and Tl salts, respectively. This distance is best considered as a weak agostic CH···M interaction[4] and may be compared with related CH···Rh and CH···Co distances of 2.4 and 2.2 Å,[5,6] respectively, in species which contain (cyclooctane-1,5-diyl)bis(pyrazolyl-η^2-borate) ligands. In the IR spectra of each of **1**, **2**, **3** and **4** there is a band at *ca.* 2870 cm^{-1} assignable to ν(CH) for this agostic CH···M moiety.

4. The average B–N distance is 1.55 Å in both the K and Tl salts. The K–N distances span the range 2.5 to 2.8 Å whereas in **2** the Tl–N distances are 2.5 Å (ave). These bond distances compare well with other K and Tl η^3- and η^2-pyrazolylborato complexes.[7,8]

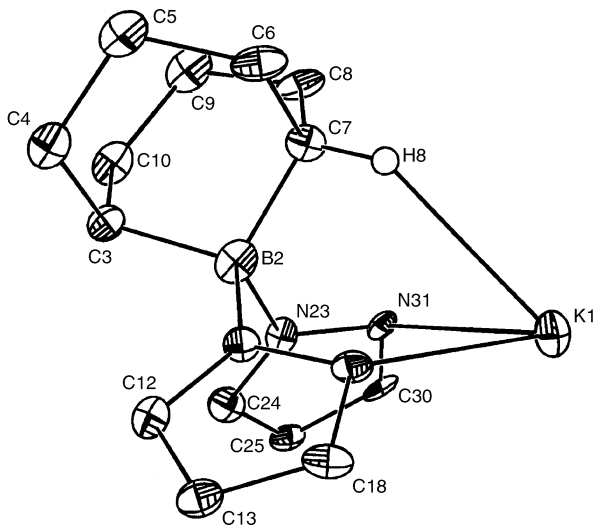
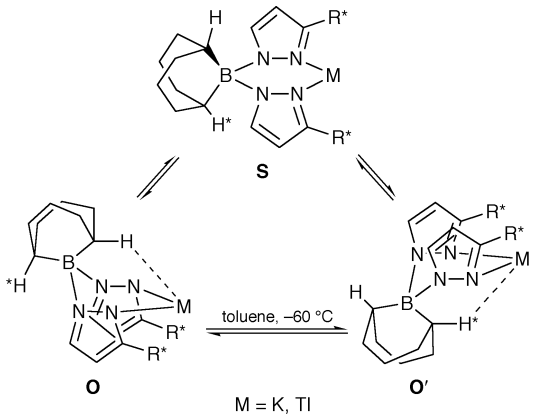


Fig. 6 An ORTEP diagram of {(cyclooctane-1,5-diyl)bis[{7(*R*)-isopropyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazolyl]borato}potassium(I)–tetrahydrofuran(1/4), **4**·4THF. The hydrogen atoms, the THF molecules and parts of the indazole are omitted. The thermal ellipsoids are of 30% probability. This view shows the twist boat like conformation of the central heterocyclic $B(NN)_2K$ ring. The weak agostic interaction between H8 and K1 is also clear in this picture.



Scheme 2 The fast exchange process depicting the facile interconversion of **O** and **O′**.

In solution the ^{1}H NMR spectra of **1**, **2** and **4** reveal only one indazolyl ligand and resonances of the cyclooctane-1,5-diyl moiety wherein the bridgehead C*H* protons and the CH_2 protons in the β-positions undergo site exchange. The same spectra are observed in toluene-d_8 or THF-d_8 even at −60 °C and below. Evidently, the molecules are fluxional and undergo a facile dynamic exchange of the type shown in Scheme 2 where in a C_2 symmetric intermediate denoted by **S** interconverts the two C_1 isomers (**O** and **O′**).

In solution a mixture of **1** with its (4*S*,7*R*)-enantiomer leads to the rapid formation of the mixed indazolyl complex, **3**. Though this scrambling of indazolyl ligands is chemically rapid, *i.e.* essentially instantaneous at room temperature, it is not rapid on the NMR time-scale. Resonances of **1** and **3** remain sharp in toluene-d_8. Thus indazolyl ligand exchange cannot be responsible for the C_2-symmetric time averaged NMR spectra of **1**, **2** and **4** noted before. Most probably this scrambling of indazolyl ligands occurs by a reversible reaction of the type shown in reaction (2) which in the presence of different pyrazole or indazole groups will lead to cross-over products. This probably accounts for the lack of success in attempted synthesis of HB(3-R′pz)$_2$(3-R′pz) which yields a mixture of products HB(3-R′pz)$_{3-n}$(3-R′pz)$_n$ where $n = 0$ to 3.

$$K(\eta^2\text{-(pz)}_2\text{BBN-9}) \rightleftharpoons K^+pz^- + \text{(pz)BBN-9} \qquad (2)$$

Conclusion

In conclusion, we have prepared a series of chiral C_1 and C_2-symmetric bidentate uninegative ligands and characterized these as their K and Tl salts. These should be useful in metathesis reactions to transfer the η^2-N_2-borate(1−) ligands to other metal centers. Based on their solid-state structures and dynamic solution behavior these could find extensive use as chiral auxiliaries in catalysis and stoichiometric organic transformations, though this matter remains to be investigated.

Experimental

General procedures

3-*tert*-Butylpyrazole, 2*H*-benz-4,5-dihydroindazole,[6] (4*S*,7*R*)-7,8,8,-trimethyl-4,5,6,7-tetrahydro-2-indazole,[4] (4*R*,7*S*)-7,8,8,-trimethyl-4,5,6,7-tetrahydro-2-indazole,[4] 7(*R*)-isopropyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2-indazole[4] and 7(*S*)-*tert*-butyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2-indazole[4] were synthesized as described before and the spectroscopic data matched to those published previously. The δ values were measured using internal deutero solvent as the reference.

A typical procedure for the synthesis of {(cyclooctane-1,5-diyl)bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κN^1,κ$N^{1'}$}potassium follows.

(4*R*,7*S*)-7,8,8,-Trimethyl-4,5,6,7-tetrahydro-2-indazole (4.4 g, 0.025 mol) was charged into a flask along with solid KOH (0.69 g, 0.0124 mol). 250 ml of freshly distilled and degassed toluene was added under N_2 atmosphere. A Soxhlet extractor which was equipped with a thimble containing powdered CaH_2 (≈5 g) was attached to the flask. The mixture was refluxed for 15 h at 150 °C during which time a white precipitate was formed. The flask was then cooled and the Soxhlet extractor was removed. 9-BBN (24.6 ml of a 0.5 solution in THF, 0.0123 mol) was added dropwise at room temperature using a syringe. After a few minutes, the precipitate dissolved and evolution of H_2 was seen. The mixture was allowed to reflux for 1 h after which time the solvent was removed *in vacuo* to give a gel like compound. Addition of hexane resulted in a fine white powder that was filtered and washed with cold hexane. NMR analysis showed the purity of the product to be >90%. Recrystallization was carried out from THF/diethyl ether solution. Yield = 2.5 g (70%). Longer reflux times and use of finely divided CaH_2 resulted in higher yields (80–85%).

Synthesis of the thallium salt, 2

Compound **1** was taken in a flask along with 1.5 equivalents of Tl(OAc) (0.77 g, 2.9 mmol) in dry CH_2Cl_2 solution. The mixture was stirred for 3 h and filtered through Celite. Evaporation of the solvent *in vacuo* gave the thallium salt as an air stable white powder. Recrystallization was carried out in THF at −20 °C. (Yield = 1.4 g, 80%)

Solution chemistry

The solution chemistry was investigated using ^{1}H NMR spectroscopy. 0.2 g of K((pz)$_2$BBN-9) was taken in 0.5 ml of toluene-d_8 and the compound was monitored over time and temperature. There was no appreciable change in the NMR spectrum over 12 h. NMR spectra was also recorded over the temperature range −60 to +60 °C. A decrease in temperature results in slight broadening of the peaks, however the exchange is still rapid at the lowest temperature. There is no appreciable line sharpening at higher temperatures.

Stability of the potassium salts

The potassium salts are air stable and can be kept in air over a period of 2–3 days. However, storing under N_2 or air over a week gave rise to decomposition (≈15% over a week).

Stability of the thallium salts

The thallium salts are stable over a longer period of time as compared to the potassium salts. Thallium salts stored over a week in air showed no appreciable decomposition as evidenced by ^{1}H NMR spectrosopy.

Attempted synthesis of (cyclooctane-1,5-diyl)-{(3-isopropyl-2*H*-pyrazol-1-yl)(2*H*-benz-4,5-dihydroindazol-2-yl)borato}potassium(I)

3-Isopropylpyrazole (2.0 g, 0.018 mol) and 1 equivalent of KOH (1.0 g, 0.018 mol) was taken in a 2-necked flask equipped with a Soxhlet apparatus. A thimble containing 5 g of CaH_2 was placed in the Soxhlet apparatus. Toluene was

Table 3 Summary of crystal data for compounds **1**, **2**, **3** · 3THF and **4** · 4THF

	1	**2**	**3**	**4**
Empirical formula	$C_{42}H_{70}BKN_4O_3$	$C_{30}H_{44}BN_4Tl$	$C_{42}H_{68}BN_4O_3K$	$C_{46}H_{80}B_1K_1N_4O_4$
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2/1$	$P2/1$	$P\bar{1}$	$P2_12_12_1$
T/°C	−168	−164	−170	−170
a/Å	11.06(2)	13.662(2)	12.445(4)	19.460(2)
b/Å	18.36(3)	33.992(5)	17.492(7)	21.273(2)
c/Å	11.12(2)	13.985(2)	11.194(4)	10.845(1)
α/°			93.05(2)	
β°	110.23(1)	119.11(1)	115.30(1)	
γ/°			69.30(2)	
V/Å^3	2119.66	5674.14	2046.89	4489.56
Molecular weight	728.95	675.90	726.94	803.08
μ/cm^{-1}	1.661	57.109	1.719	1.644
Total no. reflcns. collected	10692	22037	10955	8662
$R(F)$	0.1033	0.0766	0.0720	0.0707
$Rw(F)$	0.1067	0.0528	0.0605	0.0484

added to this flask and the mixture was refluxed overnight. After 12 h, the flask was cooled and the apparatus was dismantled. To this slurry was added a preformed mixture of 1 equivalent of 2*H*-benz-4,5-dihydroindazol-2-yl (3.1 g, 0.018 mol) and 1 equivalent of 9-BBN (36 ml of 0.5 M solution in THF) in toluene. The solution was then refluxed for 1 hour, cooled and the solvent removed *in vacuo* to give a yellow solid, which was washed with hexane and dried *in vacuo*. The solid was redissolved in THF and cooled to −20 °C. Upon cooling, white crystalline material was obtained, and the NMR analysis showed the crystals to be predominantly (cyclooctane-1,5-diyl)bis{(2*H*-benz-4,5-dihydroindazol-2-yl)-borato}potassium(I). Yield = 20%. Further concentration of the mother liquor resulted in inseparable mixtures of (cyclooctane-1,5-diyl)bis{(2*H*-benz-4,5-dihydroindazol-2-yl)-borato}potassium(I) and the title compound as evidenced by ^{1}H NMR spectroscopy.

Characterization data

{(Cyclooctane-1,5-diyl)bis[(4*R*,7*S*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κ*N*^{1},κ*N*$^{1'}$}-potassium 1. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.43 (s, 1H), 2.72 (d, 1H, J = 3 Hz), 2.53–2.29 (br, 9BBNring, 3H), 2.22–2.08 (br, 9BBNring, 2H), 1.98 (m, 1H), 1.81 (br, 9BBNring, 1H), 1.73 (vt, 1H, J = 6, 12 Hz), 1.60 (br, 9BBNring, 1H), 1.20 (m, 2H), 1.11 (s, 3H), 0.84 (m, 1H), 0.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 22 °C): δ 164.4, 124.7 124.6, 61.2, 50.1, 47.9, 35.0, 32.6, 32.6, 28.9, 25.7, 21.1, 19.8, 12.2. ^{11}B{^{1}H} NMR: δ 5.3 (s, br). IR cm^{-1} (KBr pellet): 3149.1 (w), 3060.1 (vw), 2959.2 (vs), 2926.2 (vs), 2870.0 (vs), 2837.1 (vs), 2365.0 (vw), 2331.0 (vw), 1674.0 (vw), 1563.0 (vw), 1468.0 (vs), 1445.0 (vs), 1418.0 (vs), 1390.0 (s), 1256.0 (s), 1206.0 (w), 1172.1 (w), 1088.9 (vs), 1027.2 (s), 899.1 (w), 871.0 (s), 809 (s), 709 (w), 597.0 (vw). Found: %C = 66.5, %H = 8.5, %N = 8.9. Calculated for $C_{30}H_{48}N_4BK \cdot THF \cdot 2H_2O$: %C = 66.0, %H = 8.7, %N = 9.1.

{(Cyclooctane-1,5-diyl)bis[(4*R*,7*S*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]borato-κ*N*^{1},κ*N*$^{1'}$}-thallium 2. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.29 (s, 1H), 2.61 (d, 1H, J = 4 Hz), 2.35 (br, 9BBNring, 3H), 2.19–2.16 (br, 9BBNring, 2H), 1.91 (m, 1H), 1.81 (br, 9BBNring, 1H), 1.74 (br, 9BBNring, 1H), 1.61 (t, 1H, J = 12 Hz), 1.35 (m, 1H), 1.04 (m, 2H), 0.72 (s, 3H), 0.71 (m, 3H), 0.53 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 22 °C): δ 165.4, 125.5, 125.1, 50.2, 47.5, 34.3, 33.8, 31.9, 28.1, 28.0, 25.5, 20.4, 20.3, 19.2, 19.1.

{(Cyclooctane-1,5-diyl)[(4*R*,7*S*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl][(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazol-2-yl]-borato-κ*N*^{1},κ*N*$^{1'}$}potassium 3. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.5 (s, 1H), 2.72 (d, 1H, J = 3 Hz), 2.53–2.29 (br, 9BBNring, 3H), 2.19–2.0 (br, 9BBNring, 2H), 1.90 (m, 1H), 1.81 (br, 9BBNring, 1H), 1.70 (m, 1H), 1.60 (br, 9BBNring, 1H), 1.20 (m, 2H), 1.09 (s, 3H), 0.84 (m, 1H), 0.66 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 22 °C): δ 165.0, 125.1, 124.5, 60.1, 50.2, 47.5, 35.0, 32.0, 31.3, 29.5, 25.7, 21.1, 19.8, 12.2. ^{11}B{^{1}H} NMR: δ 5.0 (s, br).

{(Cyclooctane-1,5-diyl)bis{(4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl]borato-κ*N*^{1},κ*N*$^{1'}$}potassium 4. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.63 (s, 1H), 2.73 (m, 1H), 2.42 (m, 1H), 2.31 (br, 9BBNring, 2H), 2.13 (br, 9BBNring, 2H), 1.87 (m, 1H), 1.69 (m, 1H), 1.69 (br, 9BBNring, 1H), 1.54 (br, 9BBNring, 1H), 1.43 (m, 1H) 1.17 (d, 3H, J = 7.1 Hz), 1.05 (d, 3H, J = 7.1 Hz), 0.73 (d, 3H, J = 7.1 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 22 °C): δ 149.0, 130.0, 120.2, 41.2, 32.4, 32.2, 31.8, 30.9, 27.2, 25.2, 25.1, 23.5, 23.0, 21.9, 19.2. ^{11}B{^{1}H} NMR: δ 6.0 (s, br). IR cm^{-1} (KBr pellet): 2930 (vs), 2874 (vs), 2694 (m), 2291 (m), 2224 (m), 1663 (m), 1579 (m), 1540 (m), 1456 (vs), 1423 (vs), 1373 (vs), 1339 (vs), 1261 (m), 1211 (m), 1094 (vs), 1016 (vs), 949 (s), 870 (s), 809 (s), 737 (m). Found: %C = 67.5, %H = 9.4. Calculated for $C_{30}H_{48}BN_4K \cdot H_2O$: %C = 67.7, %H = 9.0.

{(Cyclooctane-1,5-diyl)bis{(4*R*,7*R*)-7-isopropyl-4-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl]borato-κ*N*^{1},κ*N*$^{1'}$}thallium 5. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.55 (s, 1H), 2.54 (m, 1H), 2.42 (m, 1H), 2.36–2.15 (br, 9BBNring, 4H), 2.06 (m, 1H), 1.83 (br, 9BBNring, 2H), 1.75 (br, 9BBNring, 1H), 1.63 (m, 1H), 1.48 (m, 1H), 1.03 (d, 3H, J = 7.5 Hz), 0.97 (d, 3H, J = 6.9 Hz), 0.72 (d, 3H, J = 6.9 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 22 °C): δ 151.2, 131.8, 122.0, 41.3, 33.6, 33.5, 33.4, 33.1, 30.9, 28.1, 26.6, 24.0, 23.9, 23.0, 19.8. IR cm^{-1} (KBr pellet): 3211 (w), 2959 (s), 2931 (s), 2869 (s), 2752 (w), 1650 (w), 1556 (w), 1455 (s), 1416 (s), 1383 (s), 1338 (w), 1259.8 (vs), 1092 (vs), 1020 (vs), 953 (w), 804 (w), 797 (vs), 702 (w), 668 (w). Found: %C = 52.3, %H = 7.3, %N = 7.8. Calculated for $C_{30}H_{48}N_4BTl$: %C = 53.0, %H = 7.1, %N = 8.2.

{(Cyclooctane-1,5-diyl)bis[7(*S*)-*tert*-butyl-4(*R*)-methyl-4,5,6,7-tetrahydro-2*H*-indazol-2-yl)borato-κ*N*^{1},κ*N*$^{1'}$}potassium 6. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 7.73 (s, 1H), 2.59 (m, 1H), 2.44 (m, 1H), 2.42–2.38 (br, 9BBNring, 2H), 2.13–2.10 (br, 9BBNring, 3H), 1.84 (m, 1H), 1.80–1.70 (br, 9BBNring, 2H),

1.51 (br, 9BBNring, 1H), 1.35 (m, 1H), 1.23 (m, 1H), 1.12 (d, 3H, $J = 6$ Hz), 1.02 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 22 °C): δ 149.3, 129.3, 123.1, 45.6, 34.6, 34.5, 34.4, 33.8, 32.3, 29.1, 28.8, 28.5, 27.2, 26.6, 25.1, 22.3, 21.6.

(Cyclooctane-1,5-diyl)bis{3-*tert*-butyl-2*H*-pyrazol-1-yl)-borato}potassium 7. ^1H NMR (400 MHz, C_6D_6, 22 °C): δ 7.77 (d, $J = 2.1$ Hz, 1H), 6.11 (d, $J = 2.1$ Hz, 1H), 2.28 (m, br, 9BBNring, 3H), 2.10 (br, 9BBNring, 2H), 1.62 (s, 1H), 1.59 (s, 1H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 22°C): δ 159.7, 133.3, 99.8, 32.2, 31.4, 31.2. $^{11}B\{^1H\}$ NMR: δ 6.0 (s, br).

(Cyclooctane-1,5-diyl)bis{(2*H*-benz-4,5-dihydroindazol-2-yl)-borato}potassium 8. ^1H NMR (400 MHz, C_6D_6, 22 °C): δ 7.61 (s, 1H), 7.31 (d, 1H, $J = 6$ Hz), 7.13–7.07 (m, 2H, 7.02 (t, 1H, $J = 6$ Hz), 2.70–2.63 (m, 2H), 2.62–2.55 (m, 2H), 2.48–2.42 (br, 9BBNring, 3H), 2.28–2.24 (br, 9BBNring, 2H), 1.87–1.84 (br, 9BBNring, 1H), 1.73–1.70 (br, 9BBNring, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 22 °C): δ 137, 136, 130, 129, 127, 126, 122, 121, 116, 72, 59, 32, 30, 26, 19. IR cm^{-1} (KBr pellet): 2962.4 (vs), 2868 (s), 2453 (m), 1731 (m), 1555 (m), 1453 (s), 1399 (s), 1307 (s), 1261 (vs), 1096 (vs), 1018 (vs, br), 862 (s), 800 (vs), 738 (m), 715 (m), 521 (w).

(Cyclooctane-1,5-diyl)bis{(2*H*-benz-4,5-dihydroindazol-2-yl)-borato}thallium 9. ^1H NMR (400 MHz, C_6D_6, 22 °C): δ 7.49 (s, 1H), 7.39 (s, 1H), 7.10–7.01 (m, 3H), 2.61–2.56 (m, 2H), 2.50–2.45 (m, 2H), 2.39–2.27 (br, 9BBNring, 3H), 2.26–2.18 (br, 9BBNring, 2H), 1.92–1.83 (br, 9BBNring, 1H), 1.83–1.78 (br, 9BBNring, 1H).

Crystallographic studies

A summary of crystallographic data is given in Table 3 and general operating procedures and listings of programs have been given previously.[9]

CCDC reference number 440/171. See http://www.rsc.org/suppdata/nj/a9/a906582b/ for crystallographic files in .cif format.

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