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An ^{1}H and ^{13}C NMR spectroscopic study of the structure of potassium and thallium salts of tris- and tetrakis-(pyrazol-1-yl) borates in solution. Some $^{13}C-^{11}B$ and $^{13}C-^{205}Tl$ residual coupling constants

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Abstract

The ^{1}H and ^{13}C NMR spectra of 18 tris- and tetrakis-pyrazolylborates in the form of potassium or thallium salts have been recorded. Four of these compounds are new. The results are discussed with regard to two main aspects: coupling constants with ^{205}Tl and positional isomerism of the pyrazole substituents. Most borates are symmetric compounds (all the pyrazole rings being identical isomers) corresponding to less hindered structures (all 3-aryl, 3-i-propyl-4-bromo, 3-t-butyl-5-methyl or 3-t-butyl-5-i-propyl pyrazoles). Only one derivative, potassium hydrotris(2,4,6-trimethylphenylpyrazol-1-yl)borate **5**, does not fit this pattern, being either a 3/3/3 or a 3/3/5 isomer.

Keywords: ^{1}H NMR; ^{13}C NMR; Pyrazolylborates; Thallium salts; Potassium salts

1. Introduction

The interest in the coordination chemistry of polypyrazolylborate anions continues unabated [1] owing to the fact that these anions are versatile proligands useful for the preparation of complexes of elements throughout the periodic table, [2]. The characterization of their derivatives is generally based on ^{1}H and ^{13}C NMR spectroscopy, thus it is important to describe these properties carefully. In a preceding paper [3] we have reported the ^{13}C NMR spectra of a series of N*H*-pyrazoles, both in solution and in the solid state. Using the same classification, we report here ^{1}H and ^{13}C NMR spectra (mainly in solution) of some potassium (compounds **1, 3, 4, 5, 7, 12, 13** **, **15, 16,** and **17**) and thallium (compounds **2, 6, 8, 9, 10, 11, 14** and **18**) tris- and tetrakis-substituted borates (Schemes 1 and 2).

These borates, **1–18**, are shown in Scheme 2, but considering the positional isomerism (3R–5R′ vs. 3R′–5R) in the 18 compounds (since in all of them R ≠ R′), the number of possible compounds is much larger. For instance, there are four possible isomers for a tris-derivative (3/3/3, 3/3/5, 3/5/5 and 5/5/5) and five for a tetrakis derivative.

Due to the covalent nature of the pyrazolyl-thallium bond in the thallium salts, coupling constants $^{1}H-^{205}Tl$ and $^{13}C-^{205}Tl$ can be measured. These coupling constants are extremely dependent on the basicity of the pyrazolyl group and the solvent: we have only been able to measure them in $CDCl_3$, not in DMSO-d_6.

We feel it necessary to summarize the coupling to thallium in general [4,5] and, particularly, in pyrazolylborates. First, since both thallium isotopes ^{203}Tl (29.5%) and ^{205}Tl (70.5%) have the same spin ($I = 1/2$) and nearly equal gyromagnetic ratios ($\gamma^{205}Tl/\gamma^{203}Tl = 1.0096$), we will use $^{1}H-^{205}Tl$ and $^{13}C-^{205}Tl$ (the most abundant isotope) to represent both isotopes. Second, some $^{13}C-^{205}Tl$ coupling constants are amongst the largest ever measured for a given number of bonds [4,5].

The available information concerning thallium(I)

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** The borate **13** was reported after completion of this manuscript (A.J. Amoroso, A.M.C. Thompson, J.C. Jeffery, P.L. Jones, J.A. McCleverty and M.D. Ward, *J. Chem. Soc., Chem. Commun., 2751* (1994)).

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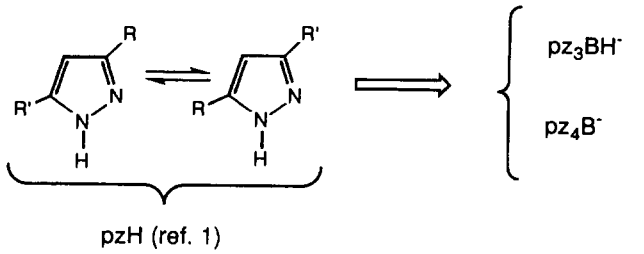
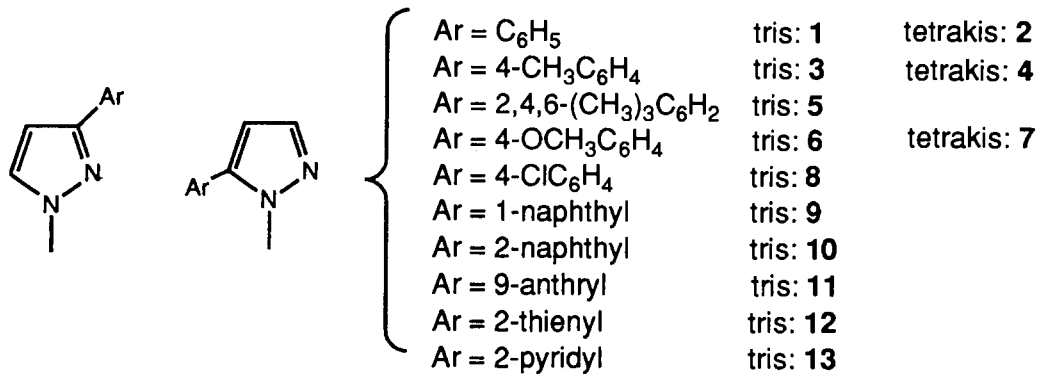


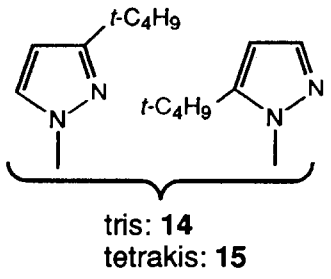
Scheme 1.

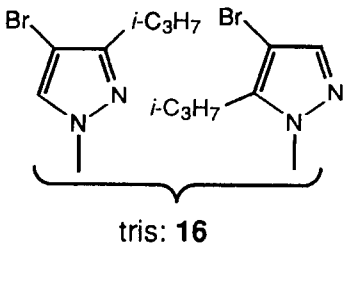
pyrazolylborates came from seven papers [6–12] of Trofimenko and coworkers and from one of Tolman et al. [2]. We have summarized (pz* is the same substituted pyrazolyl group as the one shown in detail) the reported $^{13}C-^{205}Tl$ coupling constants in Scheme 3. Compounds **20** and **22** are the thallium derivatives corresponding to the potassium salts **17** and **5**.

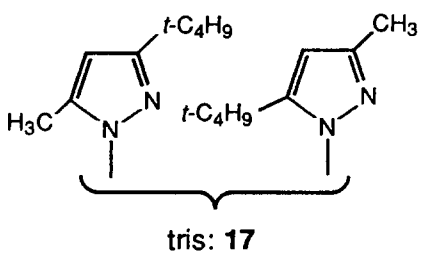
It was reported [7,9] that the introduction of a methyl group at the pyrazole 5-position of compound **14** [hydrotris(3-t-butylpyrazol-1-yl)borato]thallium(I) [6] to give [hydrotris(3-t-butyl-5-methylpyrazol-1-yl)borato]thallium(I), complex **20**, increases $^4J(^{13}C-^{205}Tl)$ of the t-butyl methyl group from 170.6 Hz to 197.4 Hz. This increase was rationalized by the greater stability of complex **20** compared with complex **14**, arising from the greater proximity of Tl to those carbon atoms. The data on complex **19** [hydrotris(3-neopentylpyrazol-1-yl)borato]thallium(I) [7] are quite different not only for the side chain but also for pyrazole carbon atoms especially, C_5. The data for **22** and **23** are taken from Refs. [10–12]. Long range couplings in compounds where the π electrons of the pyrazolyl ring can have a conjugative interaction with those of the aromatic substituents, such as in **9** and **23**, point to an extended W or M through-bond mechanism, but in derivatives such as **20**, in which this does not apply, to a predominantly through-space coupling. Finally, Tolman [2] considers that through-bond mechanisms also account for the coupling constants of **24** and **25**.

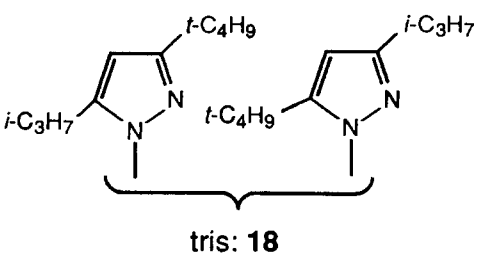
Finally, coupling constants involving bonds between elements of Group 15 of the periodic table and metals,











Scheme 2.

such as nitrogen–thallium, are affected by possible of bond-breaking. For instance, $^{1}J(^{31}P-^{107(109)}Ag)$ in $[(\eta^6\text{-p-cymene})Ru(\mu\text{-pz})_3Ag(PPh_3)]$ is sensitive to temperature, solvent and the presence of an excess of the ligand [13]. The splitting of a doublet may be smaller than the true coupling constant if there is exchange at an intermediate rate. We term these couplings "residual couplings".

2. Experimental details

2.1. Synthesis

Literature methods were used to prepare the polypyrazolylborates **1** [14], **2** [14], **3** [7], **4** [15], **5** [10], **6** [7], **7** [15], **8** [15], **11** [16], **12** [17], **14** [14], **15** [14], **16** [18], **17** [7], **19** [8], **22** [10].

2.2. Preparation of selected pyrazoles and of their hydrotris(3-Rpz)$_3$ salts

The 3(5)-substituted pyrazoles were prepared by the reaction of the appropriate acetyl-substituted aromatic compound with ethyl formate and dry sodium methoxide in toluene, similar to the preparation [14,19] of 3(5)-phenylpyrazole.

2.3. Preparation of 3(5)-(1-naphthyl)pyrazole

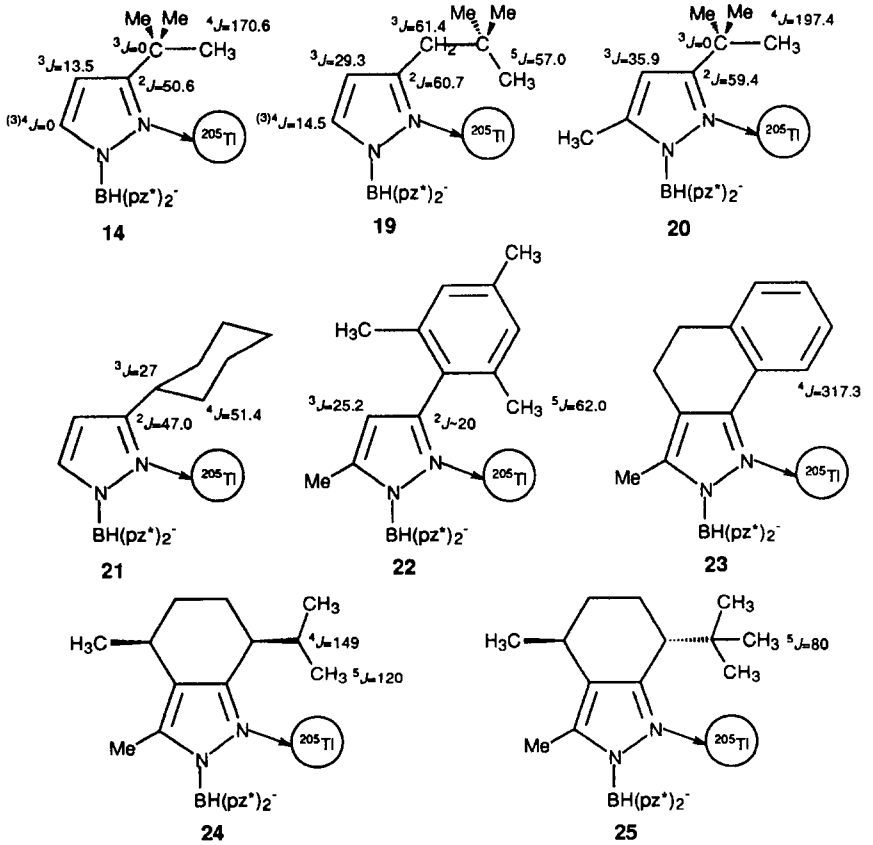
This material was purified by distillation in vacuo, collecting the fraction b.p. 190–192°C/0.6 Torr, followed by recrystallization from aqueous methanol, 66% yield; m.p. 120–121°C. Anal. Calc. for $C_{13}H_{10}N_2$: C 80.4; H 5.15; N 14.4%; found: C 80.2; H 5.31; N 14.6%.

2.4. Preparation of 3(5)-(2-naphthyl)pyrazole

This material was obtained in 81% yield and was purified by recrystallization from toluene as fine needles; m.p. 159–160°C. Anal. Calc. for $C_{13}H_{10}N_2$: C 80.4; H 5.15; N 14.4%; found: C: 80.2; H 5.34; N 14.7%.

2.5. Preparation of thallium hydrotris[3-(1-naphthyl)-pyrazol-1-yl]borate (9)

A mixture of 5.4 g (0.1 mol) KBH_4 and 97 g (0.5 mol) 3(5)-(1-naphthyl)pyrazole was stirred and heated, measuring dihydrogen evolution with a wet-test meter. When 7.5 l of dihydrogen had been evolved, the melt was cooled, dissolved in dimethylacetamide (DMAC) and stirred with an excess of $TlNO_3$. After dilution with water, extraction with methylene chloride, stripping of



Scheme 3.

Table 1
^{1}H NMR chemical shifts (ppm) and ^{1}H–^{1}H and ^{1}H–^{205}T coupling constants J (Hz) of polypyrazolylborates at 298 K

Compound no. (M salt)	H_4	H_5	J	Substituents	
1 (K salt)					
DMSO-d_6	6.50	7.50	2.1	7.78 ($H_{2',6'}$), 7.33 ($H_{3',5'}$), 7.18 ($H_{4'}$)	~4.8 (BH)
$CDCl_3$	6.62	7.62	2.3	7.75 ($H_{2',6'}$), 7.33–7.46 ($H_{3',5',4'}$)	~4.8 (BH) $^1J(^1H–^{11}B) = 100$
2 (Tl salt)					
DMSO-d_6	6.59	7.53	2.2	7.76 ($H_{2',6'}$), 7.34 ($H_{3',5'}$), 7.20 ($H_{4'}$)	
$CDCl_3$	6.65	7.77	2.4	7.74 ($H_{2',6'}$), 7.32–7.45 ($H_{3',5',4'}$)	
3 (K salt)					
DMSO-d_6	6.43	7.46	2.2	7.13 and 7.65, $^3J = 8.1$	2.28 (CH_3)
$CDCl_3$	6.40	7.28	2.1	6.95 and 7.44, $^3J = 7.9$	2.24 (CH_3) 6.1 (BH)
4 (K salt)					
DMSO-d_6	6.51	7.50	1.9	7.13 and 7.63, $^3J = 7.9$	2.28 (CH_3)
$CDCl_3$	6.33	7.26	2.2	7.07 and 7.46, $^3J = 7.9$	2.32 (CH_3)
5 (K salt)					
DMSO-d_6	5.85 (2H)	7.37 (2H)	2.0	6.81 (4H)	2.00 (2,6– CH_3) and 2.21 (4–CH_3)
	5.81 (1H)	7.43 (1H) [a]	1.5	6.78 (2H)	1.83 (2,6–CH_3) and 2.21 (4–CH_3)
$CDCl_3$	5.96 (2H)	7.44 (2H)	2.0	6.79 (4H)	1.92 (2,6–CH_3) and 2.24 (4–CH_3)
	5.95 (1H)	7.30 (1H) [a]	1.6	6.89 (2H)	1.80 (2,6–CH_3) and 2.34 (4–CH_3)
6 (Tl salt)					
DMSO-d_6	6.43	7.55	2.2	6.92 and 7.67, $^3J = 8.8$	3.75 (OCH_3)
$CDCl_3$	6.40	7.75	2.0	6.94 and 7.55, $^3J = 8.7$	3.83 (OCH_3)
7 (K salt)					
DMSO-d_6	6.44	7.55	2.0	6.71 and 7.50, $^3J = 8.7$	3.76 (OCH_3)
8 (Tl salt)					
DMSO-d_6	6.55	7.56	2.2	7.38 and 7.78, $^3J = 8.5$	
$CDCl_3$	6.50	7.83	2.1	7.42 and 7.58, $^3J = 8.5$	
$CDCl_3$ + TFA	6.94	8.12	2.7	7.48 and 7.67, $^3J = 8.6$	
CD_3COCD_3	6.60	7.87	2.2	7.42 and 7.73, $^3J = 8.5$	
9 (Tl salt)					
DMSO-d_6	6.59	7.99	1.9	[b]	
$CDCl_3$	6.53 J(Tl) = 7.5	7.98	2.0	[c]	~5.0(BH) $^1J(^1H–^{11}B) = 100$
$CDCl_3$ + TFA	7.01	8.34	2.6	[d]	
10 (Tl salt)					
DMSO-d_6	6.72	7.68	2.1	[e]	
$CDCl_3$	6.64 (br)	[f]			
11 (Tl salt)					
$CDCl_3$	6.54	8.21	2.2	[g]	
12 (K salt)					
DMSO-d_6	6.39	7.39	2.2	7.01 ($H_{4'}$), 7.24 ($H_{3'}$), 7.30 ($H_{5'}$) $J_{3',4'} = 3.5$, $J_{3',5'} = 1.1$, $J_{4',5'} = 5.0$	

13 (K salt)				
DMSO-d_6	6.69	7.58	2.1	7.19 ($H_{5'}$), 7.73 ($H_{4'}$), 7.94 ($H_{3'}$), 8.51 ($H_{6'}$) $J_{3',4'} = 7.9$, $J_{3',5'} = 1.1$, $J_{4',5'} = 7.32$, $J_{4',6'} = 1.8$, $J_{5',6'} = 4.9$
14 (Tl salt)				
DMSO-d_6	6.02	7.43	2.0	1.28
$CDCl_3$	6.04 J(Tl) = 15.7	7.54		1.36 J(Tl) = 10.4
15 (K salt)				
$CDCl_3$	6.10	7.47	2.0	1.34
16 (K salt)				
DMSO-d_6	–	7.26	–	2.88 (CH), 1.16 (2 CH_3), $J = 6.9$
17 (K salt)				
DMSO-d_6	5.76	–	–	2.10 (CH_3), 1.18 (3 CH_3)
$CDCl_3$	5.76	–	–	2.07 (br, CH_3), 1.13 (3 CH_3)
18 (Tl salt)				
$CDCl_3$	5.85 (br)	–	–	3.39 (CH), 1.10 (2 CH_3), $J = 7.0$ 1.31 (3 CH_3), ~4.9(BH)

[a] These signals belong to H_3.

[b] 8.27 (d, $H_{8'}$); 7.89 (d, $H_{5'}$); 7.87 (d, $H_{4'}$); 7.65 (d, $H_{2'}$); 7.51 (t, $H_{3'}$); 7.38 (t, $H_{6'}$); 7.05 (t, $H_{7'}$); $J_{2'3'} = 7.1$; $J_{3'4'} = 7.9$; $J_{5'6'} = 8.1$; $J_{6'7'} = 7.3$; $J_{7'8'} = 8.1$. Assignment based on a homonuclear (^{1}H–^{1}H) COSY experiment.

[c] 8.13 ($H_{8'}$ J(Tl) = 14); 7.78 (d, $H_{4'}$ and $H_{5'}$); 7.60 (br, $H_{2'}$); 7.43 (t, $H_{3'}$); 7.32 (t, $H_{6'}$); 6.98 (t, $H_{7'}$); $J_{2'3'} = 7.0$; $J_{3'4'} = 8.1$; $J_{5'6'} = 8.1$; $J_{6'7'} = 7.2$; $J_{6'8'} = 1.2$; $J_{7'8'} = 8.4$. Assignment based on a homonuclear (^{1}H–^{1}H) COSY experiment.

[d] 7.92–8.04 (m, 3H); 7.72 (dd, 1H, $^3J = 7.2$, $^4J = 0.8$); 7.46–7.60 (m, 3H).

[e] 8.29 (s, 1H, $H_{1'}$); 8.04 (dd, 1H, $^3J = 8.6$, $^4J = 1.5$, $H_{3'}$); 7.84–7.95 (m, 3H); 7.39–7.51 (m, 2H).

[f] 8.13 (s, 1H, $H_{1'}$); 7.78–7.88 (m, 4H and H-5); 7.43–7.66 (m, 2H).

[g] 8.29 (s, $H_{10'}$); 7.8 2(d, $H_{4'}$, $J_{3'4'} = 8.5$ Hz); 7.12 (ddd, $H_{3'}$, $J_{2'3'} = 6.6$ Hz, $J_{1'3'} = 1.1$ Hz), 6.58 (ddd, $H_{2'}$, $J_{1'2'} = 8.7$ Hz, $J_{2'4'} = 1.1$ Hz); 7.72 (br, $H_{1'}$). Assignment based on a homonuclear (^{1}H–^{1}H) COSY experiment.

Table 2
^{13}C NMR chemical shifts (ppm) and $^{1}H-^{13}C$ and $^{13}C-^{205}Tl$ coupling constants J (Hz) of poly(aromatic)pyrazolyl borates at 298 K

Compound no. (M salt)	C_3	C_4	C_5	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	Substituents
1 (K salt) DMSO-d_6	150.4 $^{3}J = {}^{3}J = 4.1$ $^{3}J = 8.1$ $^{2}J = 4.1$	100.9 $^{1}J = 171.6$ $^{2}J = 9.9$	134.7 $^{1}J = 182.2$ $^{2}J = 8.4$	135.3 $^{3}J = {}^{3}J = 7.4$	125.0 $^{1}J = 158.1$ $^{3}J = {}^{3}J = 6.1$	128.4 $^{1}J = 158.4$ $^{3}J = 7.5$	126.4 $^{1}J = 160.5$ $^{3}J = {}^{3}J = 7.5$	128.4 $^{1}J = 158.4$ $^{3}J = {}^{3}J = 7.5$	125.0 $^{1}J = 158.1$ $^{3}J = 6.1$	
2 (Tl salt) DMSO-d_6	151.5 $J_{C-B} \sim 4.7$	101.9 $^{1}J = 173.1$ $^{2}J = 9.6$	136.3(br) $^{1}J = 182.6$	134.5 $^{3}J = {}^{3}J = 7.3$	125.4 $^{1}J = 158.0$ $^{3}J = {}^{3}J = 6.0$	128.5 $^{1}J = 159.0$ $^{3}J = 7.0$	126.9 $^{1}J = 160.5$	128.5 $^{1}J = 159.0$ $^{3}J = 7.0$	125.4 $^{1}J = 158.0$ $^{3}J = {}^{3}J = 6.0$	
3 (K salt) DMSO-d_6	150.3	100.5 $^{1}J = 171.3$ $^{2}J = 10.1$	134.5 $^{1}J = 183.4$ $^{2}J = 8.4$	132.6 $^{3}J = {}^{3}J = 7.5$	124.9 $^{1}J = 157.4$ $^{3}J = 6.6$	129.0 $^{1}J = 156.0$	135.2 $^{3}J = {}^{3}J = 7.0$ $^{2}J = 7.0$	129.0 $^{1}J = 155.9$	124.9 $^{1}J = 157.4$ $^{3}J = 6.6$	20.8 $^{1}J = 126.3$ $^{3}J = {}^{3}J = 4.3$
4 (K salt) DMSO-d_6	150.7(br) $J_{C-B} \sim 4.1$	100.7(br) $^{1}J = 172.1$ $^{2}J = 9.5$	136.0(br) $^{1}J = 185.7$ $J_{C-B} \sim 1.5$	132.3 $^{3}J = {}^{3}J = 7.4$	125.1 $^{1}J = 157.7$ $^{3}J = 6.4$	128.9 $^{1}J = 156.1$ $J = 5.9$ $J = 5.0$	135.5 $^{3}J = {}^{3}J = 7.0$ $^{2}J = 7.0$	128.9 $^{1}J = 156.1$ $J = 5.9$ $J = 5.0$	125.1 $^{1}J = 157.7$ $^{3}J = 6.4$	20.8 $^{1}J = 126.2$ $^{3}J = {}^{3}J = 4.3$
(CP/MAS)	151.0	101.4	136.4	136.4	124.4	129.5	136.4	129.5	124.4	20.1
5 (K salt) DMSO-d_6	148.2	103.2 $^{1}J = 170.5$ $^{2}J = 10.1$	132.8 $^{1}J = 181.3$ $^{2}J = 9.1$	135.0	136.6	127.6 $^{1}J = 159.4$	137.4	127.6 $^{1}J = 159.4$	136.6	20.6 20.7 20.2 $^{1}J = 127.0$ $^{1}J = 126.5$
	138.3 $^{1}J = 178.5$ $^{2}J = 6.2$	104.9 $^{1}J = 174.4$ $^{2}J = 10.2$	144.9	133.6	136.9	127.9 $^{1}J = 160.7$	135.6	127.9 $^{1}J = 160.7$	136.9	20.6 20.7 20.2 $^{1}J = 127.0$ $^{1}J = 126.5$
6 (Tl salt)										
DMSO-d_6	150.9	101.0	135.4	127.4	126.6	113.9	158.3	113.9	126.6	55.0
$CDCl_3$	153.3(br)	103.2 $^{1}J = 175.5$ $^{2}J = 9.3$	137.0 $^{1}J = 183.6$ $^{2}J = 5.7$	126.7	128.2(br) $^{1}J = 162$	114.2 $^{1}J = 159.4$	159.3	114.2 $^{1}J = 159.4$	128.2(br) $^{1}J = 162$	55.3 $^{1}J = 143.7$
7 (K salt) DMSO-d_6	147.2	100.7 $^{1}J = 173.9$ $^{2}J = 9.9$	134.2 $^{1}J = 182.7$	121.6 $^{3}J = {}^{3}J = 7.6$	126.6 $^{1}J = 158.7$ $^{3}J = 7.7$	116.2 $^{1}J = 157.6$ $^{3}J = 4.6$	159.5 $^{3}J = {}^{3}J = 7.4$	116.2 $^{1}J = 157.6$ $^{3}J = 4.6$	126.6 $^{1}J = 158.7$ $^{3}J = 7.7$	55.1 $^{1}J = 143.7$
8 (Tl salt) $CDCl_3$, 290 K	152.5 $^{2}J(Tl) = 48.8$	103.8 $^{1}J \sim 179.1$ $^{3}J(Tl) = 24.4$	137.5(br) $^{1}J \sim 186.6$	133.7	128.2 $^{1}J = 164.1$ $^{4}J(Tl) = 124.7$ ~ 128 (vbr)	129.0 $^{1}J = 166.2$ $^{3}J = 4.9$	132.2	129.0 $^{1}J = 166.2$ $^{3}J = 4.9$	128.2 $^{1}J = 164.1$ $^{4}J(Tl) = 124.7$ ~ 128(vbr)	
$CDCl_3$, 318 K	152.8	103.8 $^{1}J = 175.4$ $^{2}J = 9.3$	137.5 $^{1}J = 184.7$ $^{2}J = 7.0$	133.8		129.1 $^{1}J = 166.1$ $^{3}J = 5.1$	132.4	129.1 $^{1}J = 166.1$ $^{3}J = 5.1$		
$CDCl_3$ + TFA	151.0	106.6 $^{1}J = 185.8$ $^{2}J = 7.6$	141.4 $^{1}J = 195.4$ $^{2}J = 7.8$	138.6	128.3 $^{1}J = 163.2$ $^{3}J = 6.9$	130.0 $^{1}J = 169.0$ $^{3}J = 5.1$	123.2	130.0 $^{1}J = 169.0$ $^{3}J = 5.1$	128.3 $^{1}J = 163.2$ $^{3}J = 6.9$	

9 (Tl salt) $CDCl_3$	151.5 ^2J(Tl) = 43.2	105.8 ^1J = 180.9 ^3J(Tl) = 23.6	136.4(br) ^1J = 189.7	[a]					
$CDCl_3$ + TFA	150.7	110.0 ^1J = 186.2 ^2J = 7.6	140.6 ^1J = 194.6 ^2J = 7.6	[b]					
10 (Tl salt) $CDCl_3$	154.0	104.0 ^1J = 174.9 ^2J = 9.2	137.4 ^1J = 185.2 ^2J = 7.5	[c]					
11 (Tl salt) $CDCl_3$	148.5 ^2J(Tl) = 33.3	107.3 ^1J = 176.1 ^3J(Tl) = 28.4	136.1(br) ^1J = 185.3 $^{(3)4}J$(Tl) = 11.3	[d]					
$CDCl_3$ + TFA	149.6	112.7	141.4	[e]					
12 (K salt) DMSO-d_6	146.0	100.9 ^1J = 173.2 ^2J = 9.9	134.5 ^1J = 183.2 ^2J = 8.5	–	138.9 $^2J = {}^3J$ = 5.8 ^3J = 9.6	122.1 ^1J = 166.1 ^2J = 5.7 ^3J = 9.4	127.4 ^1J = 167.4 ^2J = 4.4 ^2J = 4.4	123.3 ^1J = 187.0 ^2J = 7.0 ^3J = 10.0	
13 (K salt) DMSO-d_6	153.4 ^3J = 10.4 ^2J = 6.9	102.7 ^1J = 174.3 ^2J = 9.8	135.2 ^1J = 183.0 ^2J = 8.8		151.5 ^3J = 5.8 ^3J = 5.8	119.4 ^1J = 164.4 ^3J = 6.2	136.5 ^1J = 162.8 ^3J = 6.3	121.6 ^1J = 163.8 ^2J = 7.3 ^3J = 7.3	149.1 ^1J = 178.0 ^3J = 6.5 ^2J = 3.1

[a] 133.8, 131.9, 131.6 ($C_{1'}$, $C_{4'a}$, $C_{8'a}$); 128.2 (^1J = 160.9); 128.1 (^1J = 161.9); 128.1 (^1J = 161.9); 126.6 (br, ^1J = 165), 126.5 (br, ^1J = 165); 125.8 (^1J = 162.2, ^3J = 8.4); 125.2 (^1J = 162.0).
[b] 133.7, 130.4, 123.1 ($C_{1'}$, $C_{4'a}$, $C_{8'a}$), 131.9 (^1J = 161.4), 129.0 (^1J = 162.2, ^3J = 5.6), 128.7 (^1J = 161.9, ^3J = 9.2), 127.9 (^1J = 160.1, ^3J = 8.5), 126.9 (^1J = 163.5, ^3J = 7.5), 125.1 (^1J = 163.5, $C_{3'}$), 123.7 (^1J = 161.5, ^3J = 6.5).
[c] 133.5, 132.9, 131.4 ($C_{2'}$, $C_{4'a}$, $C_{8'a}$); 128.6 (^1J = 160); 128.5 (^1J = 160.0, ^3J = 4.6); 128.1 (^1J = 162.7, $^3J = {}^3J$ = 4.9); 127.7 (^1J = 161.8, $^3J = {}^3J$ = 4.7); 126.4 (^1J = 161.8, ^3J = 8.5); 126.0 (^1J = 162.3, ^3J = 8.2); 124.8 (vbr).
[d] 131.0, 128.8, 128.0 (^1J = 159.4), 127.1 (^1J = 159.0), 126.5 (^1J = 163.9), 125.6 (^1J = 159.5), 125.0 (^1J = 159.6).
[e] 131.6, 130.8, 130.7, 129.2, 128.2, 125.8, 123.3

the extracts, and trituration of the residue with methanol, afforded 60.5 g (76%) of thallium hydrotris[3-(1-naphthyl)pyrazol-1-yl]borate, m.p. 216–218°C. Anal. Calc. for $C_{39}H_{28}BN_6Tl$: C 58.9; H 3.52; N 10.6%; found: C 58.4; H 3.56; N 10.1%.

2.6. Preparation of thallium hydrotris[3-(2-naphthyl)-pyrazol-1-yl]borate (10)

This was done as above, but using 3(5)-(2-naphthyl)pyrazole instead of 3(5)-(1-naphthyl)pyrazole. After dihydrogen evolution ceased (> 7.5 l evolved), the melt was poured with rapid stirring into 600 ml toluene. A solid separated, which was filtered off hot after briefly boiling the slurry, washed with hot toluene, and air-dried. It was converted to thallium hydrotris[3-(-2-naphthyl)pyrazol-1-yl]borate which was obtained in 56 g (71%) yield. M.p. 142–146°C. Anal. Calc. for $C_{39}H_{28}BN_6Tl$: C 58.9; H 3.52; N 10.6%; found: C 59.4; H 4.07; N 10.0%.

2.7. Preparation of thallium hydrotris[3-(2-pyridyl)-pyrazol-1-yl]borate (13)

A mixture of 30 g (0.21 mol) 3(5)-(2-pyridyl)pyrazole [20] and 2.0 g (0.037 mol) KBH_4 was heated and stirred. As the pyrazole melted, dihydrogen was evolved, and after the evolution of about 2.6 l, the melt solidified. It was cooled under dinitrogen, broken up while still warm into small pieces, and stirred with 300 ml boiling toluene. The slurry was filtered hot, yielding a white solid in 12.4 g (69%) yield. The potassium salt was dissolved in DMAC, and converted to thallium hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate, which was dried, and purified by recrystallization from toluene/heptane, m.p. 283–285°C. IR (Nujol mull), BH at 2430 cm^{-1}. Anal. Calc. for $C_{24}H_{19}BN_9Tl$: C 44.4; H 2.93; N 19.4%; found: C 44.3; H 2.99; N 19.5%.

2.8. Preparation of thallium hydrotris[3-t-butyl-5-isopropylpyrazol-1-yl]borate (18)

A mixture of 50 g 3(5)-t-butyl-5(3)-isopropylpyrazole [21], and 2.5 g KBH_4 (ratio 6 : 1) was heated under reflux until no more dihydrogen was evolved, and all the KBH_4 had dissolved. The excess 3(5)-t-butyl-5(3)-isopropylpyrazole was distilled out at 1.8 Torr. The glassy residue was dissolved in DMAC and converted to the thallium salt in 63% yield, m.p. 119–121°C. IR (Nujol mull): weak BH at 2550 cm^{-1}. Anal. Calc. for $C_{30}H_{52}BN_6Tl$: C 50.6; H 7.31; N 11.8%; found: C 50.6; H 7.31; N 11.8%.

2.9. NMR spectroscopy

Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 spectrometer at 25°C unless otherwise indicated. ^1H and ^{13}C chemical shifts (ppm) are downfield from tetramethylsilane (TMS) using $CDCl_3$ ($\delta^1H = 7.26$ ppm, $\delta^{13}C = 77.0$ ppm) and DMSO-d_6 ($\delta^1H = 2.49$ ppm, $\delta^{13}C = 39.5$ ppm) as internal standards. ^1H (10^{-2} M solutions) and ^{13}C (10^{-1} M solu-

Table 3
^{13}C NMR chemical shifts (ppm) and $^1H-^{13}C$ and $^{13}C-^{205}Tl$ coupling constants J (Hz) of poly(aliphatic)pyrazolyl borates at 298 K

Compound no. (M salt)	C_3	C_4	C_5	Substituents			
14 (Tl salt)							
$CDCl_3$	163.5 $^2J(Tl) = 65.6$	101.1 $^1J = 175.1$ $^3J(Tl) = 38.6$	136.2	32.2(C)	31.8($3CH_3$) $^1J = 126.1$ $J(Tl) = 175.0$		
DMSO-d_6	162.2	100.7	135.3	31.9	31.4		
15 (K salt)							
$CDCl_3$	155(br)	101.0 $^1J = 174.0$ $^2J = 9.9$	136(br) $^1J \sim 177$	31.2(C)	30.4($3CH_3$) $^1J = 126.2$ $^3J = 4.7$		
16 (K salt)							
DMSO-d_6	153.7	89.0 $^2J = 7.3$ $^3J = 3.2$	133.5 $^1J = 187.9$	26.4(CH) $^1J = 126.4$ $^2J = 4.1$	22.0($2CH_3$) $^1J = 126.2$ $^2J = {}^3J = 5.0$		
17 (K salt)							
DMSO-d_6	158.5	100.4 $^1J = 166.9$	142.2	31.4(C)	31.0($3CH_3$) $^1J = 125.2$	11.8 $^1J = 126.8$	
$CDCl_3$	158.5	102.0	144.2 $^1J = 170.5$	31.6	30.6 $^1J = 126.0$	12.0 $^1J = 128.4$	
18 (Tl salt)							
$CDCl_3$	162.0	98.0	155.4	32.2(C)	31.8($3CH_3$) $J(Tl) = 167$	26.3(CH)	23.3($2CH_3$)

tions) chemical shifts are accurate to 0.01 and 0.1 ppm, respectively; coupling constants are accurate to ±0.2 Hz (^{1}H NMR) and to ±0.6 Hz (^{13}C NMR). Homonuclear (^{1}H–^{1}H) and heteronuclear (^{1}H–^{13}C) correlation experiments were carried out by standard procedures [22].

3. Results and discussion

Conventional mono- and two-dimensional techniques [3,23] were used to assign the different proton (Table 1) and carbon resonances (Tables 2 and 3) of compounds **1–18**.

An aspect which has complicated seriously this work was the decomposition of some pyrazolylborates when dissolved in $CDCl_3$ or DMSO-d_6; This is particularly annoying in ^{13}C NMR spectroscopy which often requires long periods for recording the spectra. The fact that these compounds decompose with release of the corresponding N*H*-pyrazole has been reported during the preparation of complexes [18]. Related to this are the examples of pyrazolylborates that rearrange during complexation (that is, starting from a 3Rpz/3Rpz/3Rpz borate, one obtains a 3Rpz/3Rpz/5Rpz complex due to a boratropic rearrangement) [24–26]. This phenomenon indicates that the N–B bond of the borate sometimes can be broken and reformed.

We have identified free N*H*-pyrazoles in the case of the following potassium salts: **3, 5, 7** and **17** (we will not report the corresponding signals in the Tables). Some potassium salts are contaminated with tenaciously retained starting pyrazole.

3.1. ^1H–^{205}Tl coupling constants

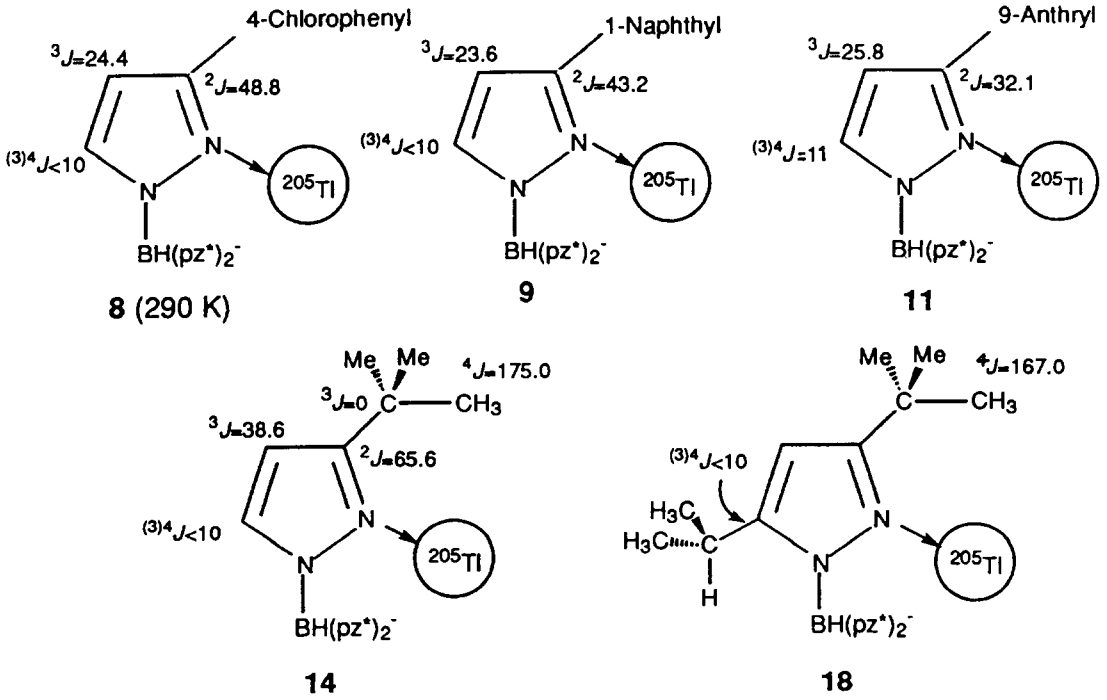
Only for two thallium derivatives, **9** and **14**, of a total of seven (**2, 6, 8, 9, 10, 11, 14, 18**) have these coupling constants been observed and this only in $CDCl_3$. Nevertheless, these are the first ^{1}H–^{205}Tl coupling constants reported for hydrotris(pyrazol-1-yl)boratothallium(I) salts. Unresolved broad signals were observed for other thallium derivatives [2].

In compound **9** ^4J = 7.5 Hz involving H_4 and ^6J = 14 Hz involving $H_{8'}$ were measured. In compound **14** ^4J = 15.7 Hz involving H_4 was the sole coupling measured. Thus, the couplings associated with H_4 are very dependent on the nature of the substituent at position 3 (1-naphthyl and t-butyl).

The coupling (and the broadening) observed in the ^{1}H NMR spectrum of **9** in $CDCl_3$ disappears upon addition of a small amount of CF_3CO_2H. The presence of catalytic amounts of this strong acid increases the rate of breaking of the thallium–nitrogen bond and the coupling vanishes.

3.2. ^{13}C–^{205}Tl coupling constants

Broad signals are common for thallium derivatives (**2, 6, 8, 9, 10, 11, 14, 18**) but coupling constants have been measured only for **9** and **14** (as in ^{1}H NMR) and for **8, 11** and **18**.



Scheme 4.

To measure the coupling constants of compound **8** the solution had to be held at 290 K. Because all these couplings correspond to more or less broad signals [13] the coupling constants in Tables 2 and 3 as well as those of Scheme 4 must be considered to be lower limits. This is certainly the case for the coupling measured on C_3 of compound **11** (a very broad signal). This also explains why the coupling constants reported for **14** in Scheme 3 [6] and Scheme 4 are different. Those reported in Ref. [6] are systematically smaller, probably because they were measured closer to the coalescence temperature.

The fact that all the compounds shown in Scheme 4 are [hydrotris(pyrazol-1-yl)borato]thallium(I) derivatives and that [tetrakis(3-phenylpyrazol-1-yl)borato]thallium **2** does not show these couplings, probably related to the fluxionality of this last compound since, although only three pyrazolyl groups are coordinated to thallium(I), an averaged spectrum is obtained for the four pyrazoles. This fluxionality involves rapid N–Tl bond breaking and bond formation, with consequent loss of coupling with ^{205}Tl.

The ability to measure $^{13}C-^{205}Tl$ coupling constants depends on the "true" value of the coupling (the larger, the easier to measure, and for this reason Scheme 4, a value for carbon C_5 of pyrazole is given as < 10 Hz, because only a broad signal is observed) but also on the rate for the N–Tl bond breaking. This rate is temperature-, field- and solvent-dependent. Probably, the compounds for which the coupling has been measured (Scheme 4) do not have larger couplings than the others ones, but have slower rates of N–Tl bond breaking.

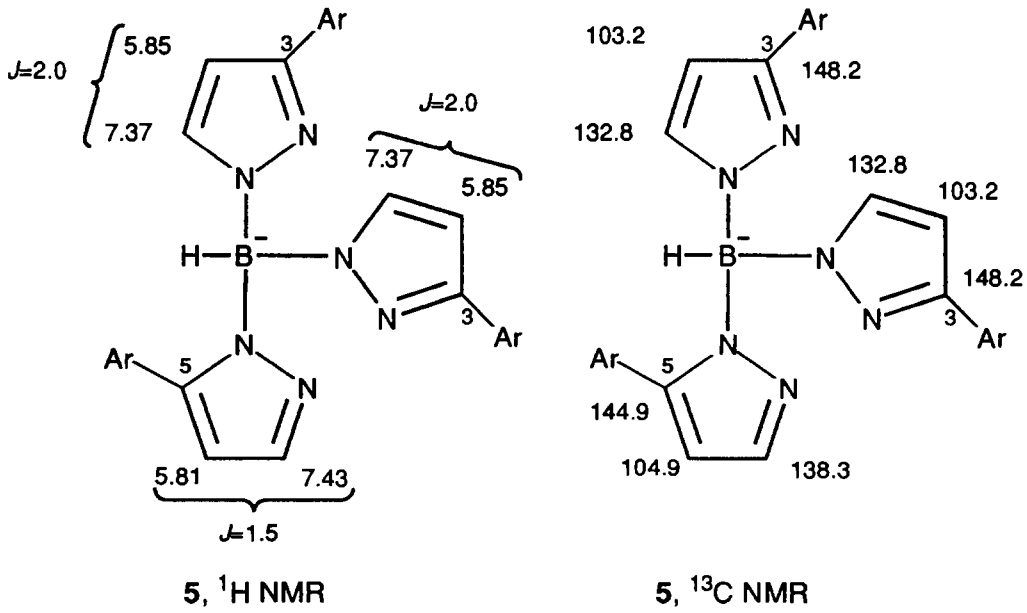
3.3. Some coupling constants with ^{11}B

Couplings similar to those reported by us for some borates derived from pyrazole itself [23] are reported in Tables 1 and 2. Compounds **1** and **9** have $^1J(^1H-^{11}B)$ couplings in the range 100–120 Hz (in tris(pyrazolyl)-borate, $^1J = 105$ Hz). In compounds **2** and **4**, we find $^3J(^{11}B-^{13}C)$ to be ~ 4.5 Hz. These couplings do not appear in hydrotris(pyrazol-1-yl)borate, but in tetrakis(pyrazol-1-yl)borate there is a $^3J(^{11}B-^{13}C)$ of 2.9 Hz [23].

3.4. Positional isomerism of pyrazolylborates

There are only three X-ray structures of the borates discussed here, **11** [16] and **14** [6]. The thallium anthryl derivative has a 3Rpz/3Rpz/3Rpz structure (in all three pyrazoles R = 9-anthryl is at position 3). The second example is also a 3Rpz/3Rpz/3Rpz derivative (R = ^{t}Bu) and the third is a 3R5R′pz/3R5R′pz/3R5R′pz derivative (R = ^{t}Bu, R′ = Me). It was generally assumed that all derivatives having no substituent at the 5-position, **1–15**, are 3Rpz/3Rpz/3Rpz derivatives [6,9]. The corresponding complexes maintain the pyrazole structure, save in the case of scorpionate **16** [9] where a 3R4Brpz/3R4Brpz/5R4Brpz complex is obtained [9,25] from a 3R4Brpz/3R4Brpz/3R4Brpz pyrazolylborate.

The results in Tables 1–3 show that most borates derived from monosubstituted pyrazoles, **1–15**, are the symmetric tris-3Rpz/3Rpz/3Rpz (**1, 3, 6, 8, 9, 10, 11, 12, 13, 14**) or tetrakis-3Rpz/3Rpz/3Rpz/3Rpz deriva-



Scheme 5.

tives (**2, 4, 7, 15**). Compound **16** is a tris-3R4Brpz/3R4Brpz/3R4Brpz-borate. The anthryl derivative **11** has very complex ^{1}H and ^{13}C NMR spectra which deserve further attention. Since the structure is known from X-ray crystallography [16], the complexity may arise from conformational differences between the anthryl residues.

The only exception is compound **5** (the mesityl derivative). The thallium complex **21**, can be isolated in two isomeric forms, the 3Rpz/3Rpz/3Rpz isomer and the 3Rpz/3Rpz/5Rpz isomer [$Tp^{Ms}Tl$, m.p. 303–305°C and $Tp^{Ms*}Tl$, m.p. 222–223°C] [10]. The compound described in this paper is the potassium salt of the 3Rpz/3Rpz/5Rpz isomer.

Selected NMR data (Tables 1 and 2) of compound **5** in DMSO-d_6 are summarized in Scheme 5 (Ar = 2,4,6-trimethylphenyl) to facilitate the discussion (the $^{1}H-^{1}H$ coupling constants of compound **21** cannot be measured due to the presence of thallium [10]. The data reported for **5** in Table 2, are roughly in a 2 : 1 intensity ratio (for the same kind of carbon atoms), for example the C_4 resonance at 103.2 ppm has an intensity twice that at 104.9 ppm. There are two pyrazoles with $^{3}J(^{1}H-^{1}H)$ of 2.0 Hz (like the remaining 3-arylpyrazoles of Table 1) and another with $^{3}J(^{1}H-^{1}H)$ of 1.5 Hz, which must be a 5-arylpyrazole derivative [13]. We have described [3] the chemical shifts in the ^{13}C NMR specific of both tautomers of 3(5)-(2,4,6-trimethyl)phenylpyrazole: it appears that both kinds of pyrazole are present in **5** in a 2(3-aryl)/1(5-aryl) ratio. We conclude that the potassium salt **5** is a tris-3Rpz/3Rpz/5Rpz derivative which is consistent with the results on one of the thallium complexes **21** [10].

Although very uncommon, there are some hydrotris(arylpyrazolyl)borates which exist as 3R/3R/5R isomers, for instance when R = mesityl, both for the potassium salt (**5**) and for one of the thallium complexes (**21**, $Tp^{Ms*}Tl$) [10]. We need to explain this experimental result. For **21**, it has been shown that 3R/3R/5R, $Tp^{Ms*}Tl$, is transformed thermally into the more stable 3R/3R/3R isomer, $Tp^{Ms}Tl$ [10]. The asymmetric isomer is therefore the kinetic product of the reaction. When the bishydrobis(3-mesitylpyrazol-1-yl)borate reacts with 3(5)-mesitylpyrazole, the last pyrazolyl residue probably as a consequence of the large 3-mesityl group has a less hindered route to replace the boron atom if it enters as a 5-mesitylpyrazole.

Compound **17** is symmetric [only one kind of pyrazole appears in the ^{1}H NMR spectrum (Table 1) and in the ^{13}C NMR spectrum (Table 2)], either as 3^{t}Bu5Mepz/3^{t}Bu5Mepz/3^{t}Bu5Mepz or as 3Me5^{t}Bupz/3Me5^{t}Bupz/3Me5^{t}Bupz. In this case, the criterion of $^{3}J(^{1}H-^{1}H)$ between proton H_4 and either proton H_3 ($J \sim 1.5$ Hz) or proton H_5 ($J \sim 2.0$ Hz) cannot be used. However, comparison with the ^{13}C chemical shifts of compound **14**, and considering the effect of a 5-methyl group [27], leaves no doubt that compound **17** is hydrotris(3-t-butyl-5-methylpyrazol-1-yl)boratopotassium, consistent with the X-ray structure of the thallium complex. In general, the ^{13}C chemical shifts of methyl pyrazole carbon atoms allows the determination of whether 3-methyl or 5-methyl groups are present [27]. However, the ^{13}C chemical shifts of hydrotris(3,5-dimethylpyrazol-1-yl)borato thallium were not useful in assigning the structure of complex **17** since its methyl resonances appear at 13.1 and 13.4 ppm in $CDCl_3$ [15]. In potassium hydrotris(3-methylpyrazoly-1-yl)borate, the 3-methyl resonance is at 13.7 ppm [28]. This also applies to compound **18**.

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References and notes

[1] (a) W.M. Vaughan, K.A. Abboud and J.M. Boncella, *J. Organomet. Chem., 485* (1995) 37; (b) G.G. Lobbia, P. Cecchi, R. Spagna, M. Colapietro, A. Pifferi and C. Pettinari, *J. Organomet. Chem., 485* (1995) 45; (c) S.J. Mason, C.M. Hill, V.J. Murphy, D. O'Hare and D.J. Watkin, *J. Organomet. Chem., 485* (1995) 165; (d) V.S. Joshi, K.M. Sathe, M. Nandi, P. Chakrabarti and A. Sarkar, *J. Organomet. Chem., 485* (1995) C1.

[2] D.D. LeCloux, C.J. Tokar, M. Osawa, R.P. Houser, M.C. Keyes and W.B. Tolman, *Organometallics, 13* (1994) 2855.

[3] C. López, R.M. Claramunt, S. Trofimenko and J. Elguero, *Can. J. Chem., 71* (1993) 678.

[4] J.F. Hinton, *Magn. Reson. Chem., 25* (1987) 659.

[5] J.F. Hinton, K.R. Metz and R.W. Briggs, *Prog. Nucl. Magn. Reson. Spectrosc., 20* (1988) 423.

[6] A.H. Cowley, R.L. Geerts, C.M. Nunn and S. Trofimenko, *J. Organomet. Chem. 365* (1989) 19.

[7] S. Trofimenko, J.C. Calabrese, J.K. Kochi, S. Wolowiec, R.B. Hulsbergen and J. Reedijk, *Inorg. Chem., 31* (1992) 3943.

[8] J.C. Calabrese and S. Trofimenko, *Inorg. Chem. 31* (1992) 4810.

[9] S. Trofimenko, *Chem. Rev., 93* (1993) 943.

[10] A.L. Rheingold, C.B. White and S. Trofimenko, *Inorg. Chem., 32* (1993) 3471.

[11] A.L. Rheingold, B.S. Haggerty and S. Trofimenko, *Angew. Chem., Int. Ed. Engl., 33* (1994) 1983.

[12] A.L. Rheingold, R.L. Ostrander, B.S. Haggerty and S. Trofimenko, *Inorg. Chem., 33* (1994) 3666.

[13] D. Carmona, J. Ferrer, M.P. Lamata, L.A. Oro, H.H. Limbach, G. Scherer, J. Elguero and M.L. Jimeno, *J. Organomet. Chem., 470* (1994) 271.

[14] S. Trofimenko, J.C. Calabrese and J.S. Thompson, *Inorg. Chem., 26* (1987) 1507.

[15] S. Trofimenko, unpublished work.

[16] R. Han, G. Parkin and S. Trofimenko, *Polyhedron, 14* (1995) 387.

[17] J.C. Calabrese, P.J. Domaille, S. Trofimenko and G.J. Long, *Inorg. Chem., 30* (1991) 2795.

[18] M. Cano, J.A. Campo, J.V. Heras, E. Pinilla, C. Rivas and A. Monge, *Polyhedron, 13* (1994) 2463.
[19] J. Elguero and R. Jacquier, *Bull. Soc. Chim. Fr.*, (1966) 2832.
[20] (a) M. Tisler, B. Stanovnik and B. Vercek, *Vest. Slov. Kem. Drus., 27* (1980) 65; (b) idem, *Chem. Abstr., 93* (1980) 204527g.
[21] J. Elguero, R. Jacquier and H.C.N. Tien Duc, *Bull. Soc. Chim. Fr.*, (1966) 3727.
[22] W.R. Croasmun and R.M.K. Carlson, *Two-Dimensional NMR Spectroscopy*, 2nd ed., VCH, Weinheim, 1994.
[23] C. López, R.M. Claramunt, D. Sanz, C. Foces-Foces, F.H. Cano, R. Faure, E. Cayón and J. Elguero, *Inorg. Chim. Acta, 176* (1990) 195.
[24] M. Cano, J.V. Heras, S. Trofimenko, A. Monge, E. Gutierrez, C.J. Jones and J.A. McCleverty, *J. Chem. Soc., Dalton Trans.*, (1990) 3577.
[25] S. Trofimenko, J.C. Calabrese, P.J. Domaille and J.S. Thompson, *Inorg. Chem., 26* (1989) 1091.
[26] J.C. Calabrese, P.J. Domaille, J.S. Thompson and S. Trofimenko, *Inorg. Chem., 29* (1990) 4429.
[27] M. Begtrup, G. Boyer, P. Cabildo, C. Cativiela, R.M. Claramunt, J. Elguero, J.I. García, C. Toiron and P. Vedsø, *Magn. Reson. Chem., 31* (1993) 107.
[28] P. Cecchi, G.G. Lobbia, F. Marchetti, G. Valle and S. Calogero. *Polyhedron, 13* (1994) 2173.