

A multinuclear NMR study in the solid state and in solution of thallium(I) tris-(pyrazol-1-yl)borates (thallium scorpionates)

Rosa M. Claramunt^{a,*}, Dionisia Sanz^a, M. Dolores Santa María^a,
José Elguero^b, Swiatoslaw Trofimenko^c

^a Departamento de Química Orgánica y Biología, Facultad de Ciencias, UNED, Senda del Rey 9, E-28040 Madrid, Spain

^b Instituto de Química Médica, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain

^c Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522, USA

Received 4 July 2003; accepted 24 September 2003

Abstract

The ¹H, ¹³C and ¹⁵N NMR spectroscopic properties of six thallium tris-(pyrazol-1-yl)borates, including a tetrakis derivative, were determined. The results in solution were necessary to understand those, more complicated, in the solid state. A collection of ²⁰⁵Tl–¹⁵N and ²⁰⁵Tl–¹³C couplings was measured in the latter state. Among those, a very large coupling constant (between 194 and 282 Hz) has been measured on the carbon at the position 4 of the pyrazole ring in several compounds and particularly for the cyclobutyl derivative [Tl(Tp^{Cbu})]. It has been assigned to a direct interaction of the 4-C–H···Tl type and related to the X-ray structures, when available.

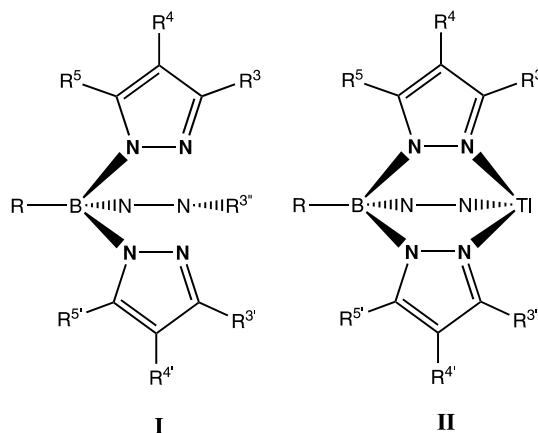
© 2003 Elsevier B.V. All rights reserved.

Keywords: Pyrazolylborates; Thallium; ¹H NMR; ¹³C NMR; ¹⁵N NMR; CPMAS

1. Introduction

Scorpionates **I** are a family of very popular ligands [1]. The main classes are tris-pyrazolylborates (R = H) and tetrakis-pyrazolylborates (R = pyrazole). The different pyrazole rings could be identical or different. There is a great variety of metal that have been coordinated to scorpionates [1], one of them being thallium(I) pyrazolylborates **II** [2,3]. We have devoted some effort to the characterization of these last compounds by multinuclear NMR thus determining, for the first time, some residual ¹³C–¹¹B and ²⁰⁵Tl–¹³C coupling constants [4] and, using a ¹⁵N labeled derivative, the corresponding ²⁰⁵Tl–¹⁵N couplings as well as the ²⁰⁵Tl chemical shifts [5]. We demonstrated that these couplings are temperature and solvent dependent due to a dynamic process involving the cleavage of the N–Tl bond. Much caution needs the determination of ²⁰⁵Tl–¹H and ²⁰⁵Tl–¹³C coupling constants in solution. The “observed” or

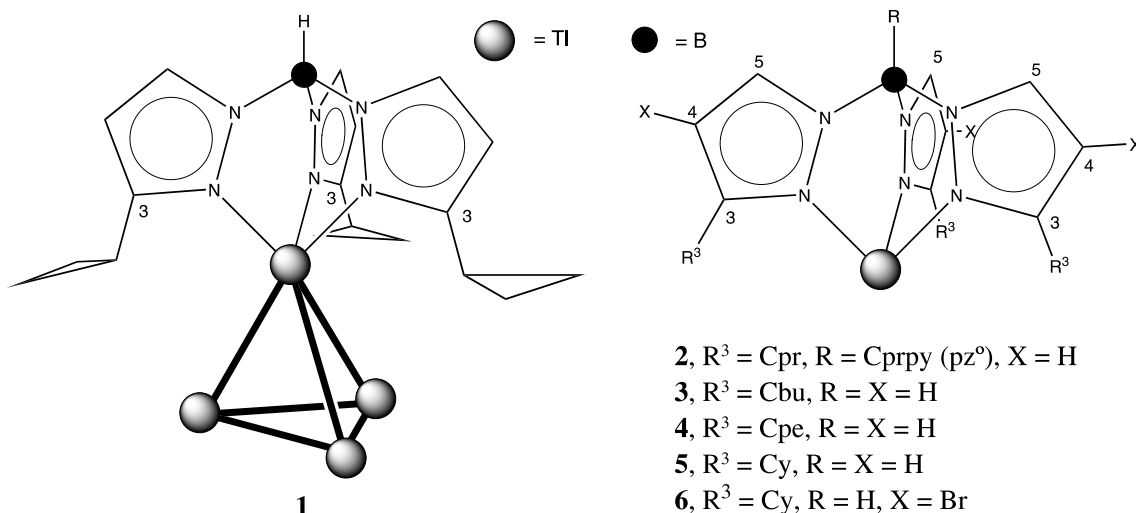
“apparent” coupling constant can differ considerably from the “true” values, due to both a dynamic process involving thallium dissociation and to the spin-lattice relaxation of the thallium [6], making them solvent, temperature and spectrometer field dependent.



In the present publication we will report the study of six compounds (1–6, Scheme 1) where the ligands are

* Corresponding author. Tel.: +91-398-7322; fax: +91-398-6697.

E-mail address: rclaramunt@ccia.uned.es (R.M. Claramunt).



Scheme 1. The six compounds under study.

formed by 3-cycloalkylpyrazoles (from cyclopropyl to cyclohexyl). The ¹H and ¹³C NMR in CDCl₃ solution of these compounds have already been reported but the assignments were incomplete: **1** [7,8], **2** [8], **3** [9], **4** [9], **5** [10,11] and **6** [11].

2. Experimental

2.1. Chemicals

All the compounds discussed in this paper have been previously described [7–11].

2.2. NMR measurements

NMR spectra were recorded on a Bruker DRX 400 (9.4 T, 400.13 MHz for ¹H, 100.62 MHz for ¹³C and 40.56 MHz for ¹⁵N) spectrometer. Chemical shifts (δ in ppm) are given from internal solvent CDCl₃ 7.26 for ¹H and 77.0 for ¹³C, DMSO-*d*₆ 2.49 for ¹H and 39.5 for ¹³C. 2D inverse proton detected heteronuclear shift correlation spectra, HMBC, were obtained using the standard pulse sequences [12] for ¹⁵N NMR and nitromethane was used as external standard. No corrections for bulk differences were applied [13]. Coupling constants (*J* in Hz) are accurate to ± 0.2 Hz for ¹H and ¹³C and ± 0.6 Hz for ¹⁵N. ¹³C CPMAS NMR spectra (100.74 and 125.77 MHz) have been recorded on Bruker WB400 and DSX500 instruments at 300 K using a 4 mm probehead and rotational frequencies of about 10–12 kHz. ¹⁵N CPMAS NMR (20.28 MHz) spectra have been obtained on a Bruker AC-200 spectrometer at 298 K using a 7 mm probehead that achieves rotational frequencies of 3.5–4.5 kHz. Samples were carefully packed in ZrO₂ rotors and the standard CPMAS sequence was

employed. Chemical shifts (δ) in ppm are referred to Me₄Si and ¹⁵NH₄Cl [these were converted to nitromethane using the relationship: δ ¹⁵N(nitromethane) = δ ¹⁵N(ammonium chloride) – 338.1, all values in ppm]. In the case of compound **3** (see Fig. 2) a ¹³C CPMAS NMR spectrum has been recorded at 50 MHz on a Bruker AC-200 instrument.

3. Results and discussion

We report the solution results in Table 1 and the solid-state data (CPMAS) in Table 2.

Generally, the signal of the proton bound to boron is too broad to be measured ¹*J*(H,B) [7–11] but in some cases, an approximate value of the coupling can be estimated to be about 120 Hz, for instance using ¹¹B NMR [14,15]. The signal, formally the superposition of a quadruplet (¹¹B: natural abundance 80.42%, *I* = 3/2, γ = 8.5827 in 10⁷ rad T⁻¹ s⁻¹ units) and a septuplet (¹⁰B: natural abundance 19.58%, *I* = 3, γ = 2.8747 in 10⁷ rad T⁻¹ s⁻¹ units) appears as a distorted quadruplet because the septuplet due to ¹⁰B is not observed. Its minor intensity (19.58%) and the smaller value of the coupling constant (0.335 times that with ¹¹B) [15] made its direct observation very difficult. To estimate ¹*J*(¹¹B,¹H) we take into account that in a partially relaxed quadruplet, the outer lines move towards the inner lines which remain almost constant in their position until the splitting is collapsed. Therefore, the distance of the inner lines have been taken as the coupling constant (see Fig. 1 for the case of compound **1** in CDCl₃).

Some ²⁰⁵Tl–¹³C coupling constants were reported for compounds **5** and **6** in CDCl₃ [10,11] but the value of these couplings should be taken with caution as we [4] and others [6] have pointed out. For instance, we have

Table 1
¹H and ¹³C NMR data (δ in ppm, J in Hz) of scorpionates **1–6** in solution

Comp.	Tris/tetrakis	Subs.	Solvent	¹ H NMR			¹³ C NMR			
				Pyrazole		Subs.	Pyrazole			Subs.
				Pos. 4	Pos. 5		Pos. 3	Pos. 4	Pos. 5	
1	Tris	Cpr	CDCl ₃	5.78 (d) <i>J</i> = 1.9	7.53 (d) <i>J</i> = 1.9	2.08 (1'-H) 0.97 (2H) 0.70 (2H) ^a	156.0 (br)	99.8 ¹ <i>J</i> = 172.4 ² <i>J</i> = 8.9	136.0 ¹ <i>J</i> = 183.8 ² <i>J</i> = 6.0	9.1 (br, 1'-C) ¹ <i>J</i> = 158.5 8.0 (br, 2', 3'-C) ¹ <i>J</i> = 161.7
1	Tris	Cpr	DMSO-d ₆	5.79 (d) <i>J</i> = 2.1	7.51 (d) <i>J</i> = 2.1	2.11 (1'-H) 0.92 (2H) 0.59 (2H) ^b	155.5	99.3 ¹ <i>J</i> = 173.4 ² <i>J</i> = 10.0 ³ <i>J</i> = 2.9	135.9 ¹ <i>J</i> = 184.2 ² <i>J</i> = 8.0	8.9 (1'-C) ¹ <i>J</i> = 161.6 8.3 (2', 3'-C) ¹ <i>J</i> = 162.3
2	Tetrakis	Cpr	CDCl ₃	5.86 (d) <i>J</i> = 2.4	7.41 (d) <i>J</i> = 2.4	2.05 (1'-H) 0.95 (2H) 0.71 (2H)	156.8 ³ <i>J</i> (B) = 3.7	101.2 ¹ <i>J</i> = 173.4 ² <i>J</i> = 8.8	136.1 ¹ <i>J</i> = 185.2 ² <i>J</i> (B) = 3.5	9.1 (1'-C) ¹ <i>J</i> = 161.1 8.0 (2', 3'-C) ¹ <i>J</i> = 160.8
2	Tetrakis	Cpr	DMSO-d ₆	5.79 (d) <i>J</i> = 2.3	6.88 (d) <i>J</i> = 2.3	2.02 (1'-H) 0.86 (2H) 0.59 (2H)	155.8 ³ <i>J</i> (B) = 4.2	99.6 ¹ <i>J</i> = 172.4 ² <i>J</i> = 9.4	135.1 ¹ <i>J</i> = 184.0 ² <i>J</i> (B) = 4.3	9.2 (1'-C) ¹ <i>J</i> = 161.9 8.3 (2', 3'-C) ¹ <i>J</i> = 161.7
3	Tris	Cbu	CDCl ₃	6.12 (d) <i>J</i> = 2.1	7.60 (d) <i>J</i> = 2.1	3.73 (1'-H) 2.41 (2H) 2.23 (2H) 2.07 (1H) 1.93 (1H) ^c	157.9	101.6 ¹ <i>J</i> = 173.1 ² <i>J</i> = 8.5	136.0 ¹ <i>J</i> = 183.9 ² <i>J</i> = 7.1	33.9 (1'-C) ¹ <i>J</i> = 133.7 30.0 (2', 4'-C) ¹ <i>J</i> = 135.2 18.9 (3'-C) ¹ <i>J</i> = 135.0
4	Tris	Cpe	CDCl ₃	6.03 (d) <i>J</i> = 2.0	7.57 <i>J</i> = 2.0	3.26 (1'-H) 2.12 (2H) 1.69 (2H) 1.80 (2H) 1.69 (2H) ^d	158.0	101.2 ¹ <i>J</i> = 172.9 ² <i>J</i> = 6.4	135.8 ¹ <i>J</i> = 183.9 ² <i>J</i> = 7.0	38.9 (1'-C) ¹ <i>J</i> = 128.3 34.1 (2', 5'-C) ¹ <i>J</i> = 128.7 25.4 (3', 4'-C) ¹ <i>J</i> = 130.5
5	Tris	Cy	CDCl ₃	6.01 (d) <i>J</i> = 2.0	7.55 (d) <i>J</i> = 2.0	2.82 (1'-H) 1.97 (1H) 1.45 (1H) 1.86 (1H) 1.45 (1H) 1.76 (1H) 1.30 (1H) ^e	159.2	100.9 ¹ <i>J</i> = 173.4 ² <i>J</i> = 7.9	135.8 ¹ <i>J</i> = 183.1 ² <i>J</i> = 7.8	37.6 (1'-C) ¹ <i>J</i> = 128.0 34.2 (2', 6'-C) ¹ <i>J</i> = 129.3 26.6 (3', 5'-C) ¹ <i>J</i> = 129.3 26.2 (4'-C) ¹ <i>J</i> = 127.2
5	Tris	Cy	DMSO-d ₆	6.01 (d) <i>J</i> = 2.1	7.53 (d) <i>J</i> = 2.1	2.82 (1'-H) 1.85 (1H) 1.35 (1H) 1.75 (1H) 1.35 (1H)	158.6	100.9	135.6	36.6 (1'-C) 33.7 (2', 6'-C) 26.0 (3', 5'-C) 25.6 (4'-C)

Table 1 (continued)

Comp.	Tris/tetrakis	Subs.	Solvent	¹ H NMR		¹³ C NMR							
				Pyrazole		Subs.		Pyrazole		Subs.			
				Pos. 4	Pos. 5	Pos. 3	Pos. 4	Pos. 5	Pos. 3	Pos. 4	Pos. 5		
6	Tris	Cy ₂ 4Br	CDCl ₃	(Br)	7.57	1.66 (1H)	156.4 (br)	91.0 (br)	136.7	37.3 (1'-C)			
						1.21 (1H) ^f					⁴ J(Tl) = 144.8		
						2.83 (1'-H)							
						1.90 (1H)							
						1.67 (1H, br)							
						1.90 (1H)							
1.37 (1H)													
6	Tris	Cy ₂ 4Br	DMSO-d ₆	(Br)	7.23	1.81 (1H)	153.0	89.0	133.4	36.1 (1'-C)			
						1.37 (1H) ^g					31.8 (2', 6'-C)		
						2.55 (1'-H)						26.1 (3', 5'-C)	
						1.76 (1H)							25.7 (4'-C)
						1.49 (1H)							
						1.74 (1H)							
1.29 (1H)													
1.65 (1H)													
						1.21 (1H) ^h							

The BH: ^aδ = 4.43 (q, br), ¹J_{BH} = 124 (see Fig. 1); ^bδ = 4.32 (s, br); ^cδ = 4.51 (q, br), ¹J_{BH} = 124; ^dδ = 4.58 (q, br), ¹J_{BH} = 124; ^eδ = 4.50 (q, br), ¹J_{BH} = 111; ^fδ = 4.40 (s, br); ^gδ = 4.30 (q, br), ¹J_{BH} = 111; ^hδ = 4.40 (s, br).

found a doublet for the signal at 33.2 ppm (2'-C) of **6** in CDCl₃ (Table 1) with an apparent coupling of 144.8 Hz (Bruker DRX-400). For the same compound in the same solvent a value of 50 Hz was reported in reference [11] for the signal at 32.8 ppm (2'-C, Nicolet NT360WB). In Table 1 some ¹³C–¹¹B couplings are reported for compound **2**; note that this compound is the only tetrakis derivative, couplings with quadrupolar nuclei being very sensitive to symmetry; a similar observation was made for thallium tetrakis-(pyrazol-1-yl)borate itself [15]. This compound presents in ²⁰⁵Tl NMR an intense signal at 2045.2 ppm and a series of small ones (solvent CDCl₃) [16]. We have reported a value of 2210.2 ppm for [Tl(Tp^{Me2})] [5] and Parkin and coworkers [6] a value of 2208 ppm for the same compound and 2021 ppm for Tl(Tp^{But}).

The remaining chemical shifts and coupling constants of Table 1 have classical values and do not deserve further comments. The systems formed by the protons of the cycloalkyl substituents have been analyzed but only the chemical shifts are reported in Table 1. For instance, the ¹H NMR spectra of the cyclopropyl substituent in compounds **1** and **2** appears as an AA'BB'X system that was analyzed using the program Bruker Win-Daisy 3.0: see Scheme 2 for compound **1**. Those for compound **2** are nearly identical. The assignment of protons A and B is based on the values of *J*_{cis} and *J*_{trans}.

The solid state ¹³C NMR spectra of Table 2 are difficult to interpret due to the presence of several different pyrazole moieties (either differences between the pyrazoles of the same molecule or differences between different molecules in the crystal). Moreover, the quadrupolar ¹⁴N nucleus at position 2 in some cases split the signal of 3-C [17]. Nevertheless, the ²J(²⁰⁵Tl, ¹³C) of the carbon atom at 3-C and the ³J(²⁰⁵Tl, ¹³C) of the carbon 4-C have been measured several times (Scheme 3, all values in Hz). The first one has values between 40 and 65 Hz while the second one is smaller, between 35 and 60 Hz. The ³J(²⁰⁵Tl, ¹³C) coupling of carbon 5-C is usually still smaller (less than 10 Hz) and difficult to observe [4]. Some ²⁰⁵Tl–¹³C couplings of the cycloalkyl substituents have also been measured and assigned to classical (through bonds) couplings although direct couplings (through space) cannot be excluded. We have summarized in Scheme 3 the ²⁰⁵Tl–¹³C couplings in scorpionates.

The signal of the 4-C of compound **3** (101.0 ppm) is totally unexpected: besides a normal ³J(²⁰⁵Tl, ¹³C) of 35 Hz (see [4] for other values in this range), there is a very large coupling of 233 Hz. We consider that the signal corresponds the X part (¹³C) of an ABX system (A and B, ²⁰⁵Tl nuclei) that looks like a doublet of doublets (actually six signals are expected but two could be of very low intensity). The fact that the signal is a doublet of doublets (at 101.0 ppm) and not two doublets (*J* = 35 Hz) corresponding to two different

Table 2
 ^{13}C NMR data (δ in ppm, J in Hz) of scorpionates **1–6** in the solid state

Comp.	Tris/tetrakis	Subs.	Pyrazole					Substituent	
			Pos. 3 (δ)	Pos. 3 (J)	Pos. 4 (δ)	Pos. 4 (J)	Pos. 5	δ	J
1	Tris	Cpr	156.6	$^2J(\text{TI}) = 40$	97.4	$^3J(\text{TI}) = 34, J(\text{TI}) = \mathbf{282}$	134.6	10.1 (1'-C)	$^3J(\text{TI}) = 163$
			156.4		101		136	8.3 (2', 3'-C)	
2	Tetrakis	Cpr	156.3		97.4	$^3J(\text{TI}) = 58, J(\text{TI}) = \mathbf{263}$	133.8	7.27–12.9 (1', 2', 3'-C)	
			158.4		98.1		135.1		
3	Tris	Cbu	159	$^2J(\text{TI}) = 62$	101	$^3J(\text{TI}) = 35, J(\text{TI}) = \mathbf{233}$	135.8	33.7 (1'-C)	$^3J(\text{TI}) = 97$
								31.0 (2'-C)	
4	Tris	Cpe	154.3	$^2J(\text{TI}) = 67$	101.8	$^3J(\text{TI}) = 42, J(\text{TI}) = \mathbf{194}$	134.1	39.2 (1'-C)	$^3J(\text{TI}) = 107$
			156.4		102.5		134.9	39.7 (1'-C)	
5	Tris	Cy	157.8	$^2J(\text{TI}) = 53$	103.3		135.8	40.2 (1'-C)	$^3J(\text{TI}) = 131$
							137	30.9 (2' or 5'-C)	
6	Tris	Cy,4Br	158.6	$^2J(\text{TI}) = 52$	100.5	$^3J(\text{TI}) = 39$	133.3	34.2 (1'-C) ^a	$^3J(\text{TI}) = 102$
			159.5		102.9		135.6	35.1 (2', 6'-C)	
6	Tris	Cy,4Br	155.5		90.7		136.7	38.0 (1'-C) ^b	$^3J(\text{TI}) = 93$
			156.9		92.3			34.7 (2', 6'-C)	
				93.8			27.6 (3', 5'-C)		
							26.3 (4'-C)		

^a In some cases, these values correspond to average signals: 1'-C, 32.0 (84 Hz), 34.3 (101 Hz), 36.3 (119 Hz); 3', 5'-C, 26.9, 26.3.

^b In some cases, these values correspond to average signals: 2', 6'-C, 34.2 (199 Hz), 34.2 (199 Hz), 35.0, 35.4; 4'-C, 25.6, 26.5, 26.9.

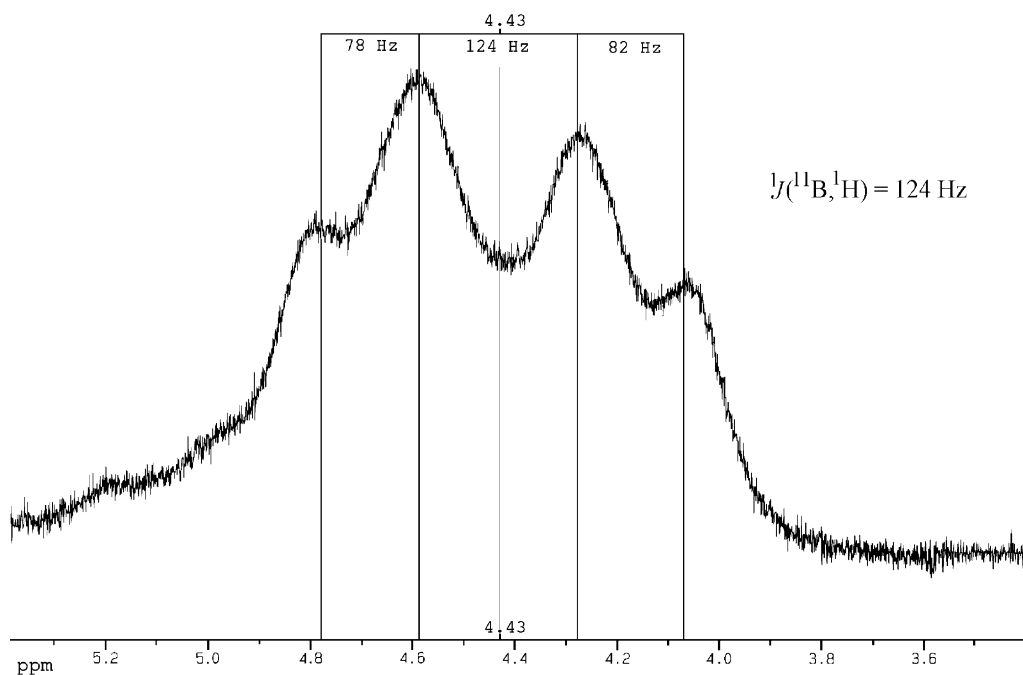
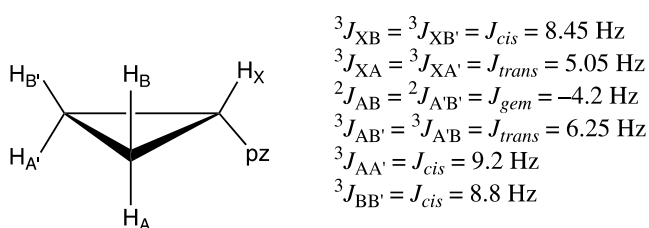


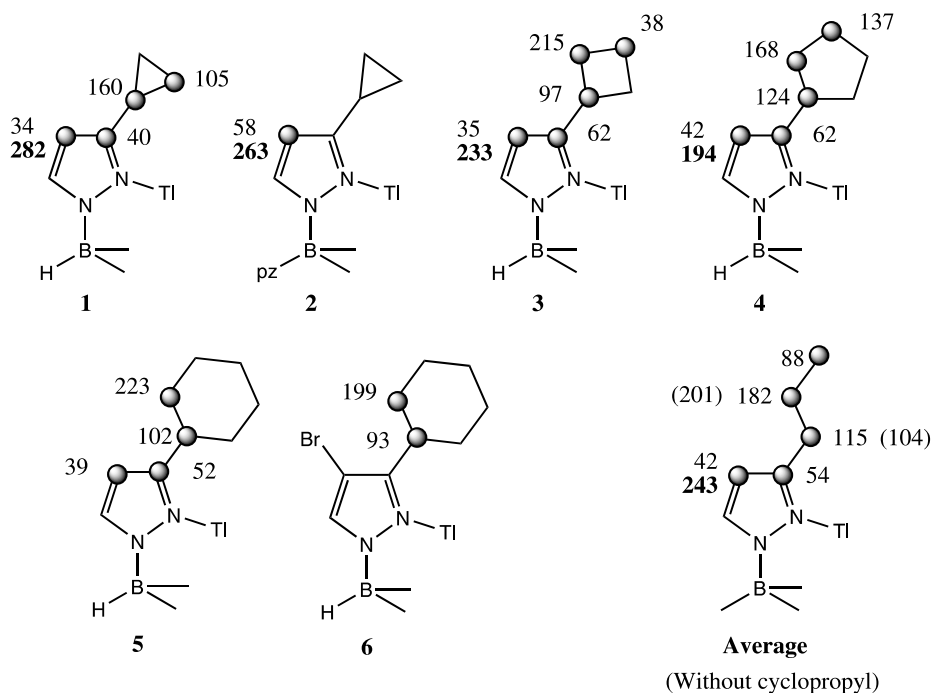
Fig. 1. ^1H NMR partial spectrum of compound **1** in CDCl_3 at 400.13 MHz: signal of the B–H proton; solvent CDCl_3 (see Table 1).



Scheme 2. Computer fitting of the AA'BB'X system.

signals, was proved by recording the spectra at 50 and 125 MHz (Fig. 2). We do not think that the field effects described by Parkin [6] are relevant here because they do not affect the chemical shifts only the coupling constants.

This coupling was found for some of the 4-C signals of **1**, **2** and **4**. It was first assigned to a $^4J(^{205}\text{Tl}, ^{13}\text{C})$ between 4-C and a second thallium atom [a 4-C-3-C-2-N-Tl-Tl



Scheme 3. ^{205}Tl – ^{13}C Couplings in compounds **1**–**6** [bold figures, direct $J(^{205}\text{Tl}, ^{13}\text{C})$].

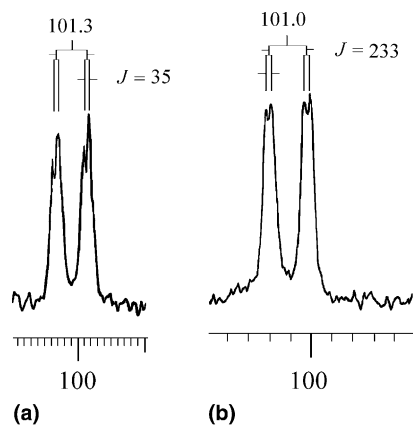


Fig. 2. The ^{13}C CPMAS NMR signal of 4-C in compound **3** recorded at (a) 50 MHz, (b) 125 MHz.

coupling] in the crystalline solid. But, with the exception of compound **1** where they are short Tl–Tl distances [7,8], in the remaining compounds [8–11], and particularly, in **3** the Tl–Tl distances are very long (above 8 Å). The only other reasonable hypothesis is a direct ^{205}Tl – ^{13}C coupling between the 4-C carbon atom of a molecule and the nearest thallium atom of another molecule. This would explain why the coupling disappears in solution. A related observation has been made by Janiak in the case of a molecular $\text{C}_5(\text{CH}_2\text{Ph})_5\text{Tl}$ complex in solution

where the *ortho*-phenyl carbon also shows a unusually large Tl–C coupling constant of 43 Hz [18]; the X-ray structure reveals the spatial proximity of both atoms [19]. There is also a report in the literature concerning the observation of very large ^{205}Tl – ^{19}F coupling constants in the non-bonded structure of a cage compound ($\text{F}\cdots\text{Tl}$ distance, about 3 Å) [20]. Janiak and coworkers [21] have recently reported the structure of the parent thallium tris-(pyrazol-1-yl)borate and reported some Tl \cdots C short distances.

Table 3 reports our results both in solution and in the solid state concerning ^{15}N NMR (always in natural abundance). The coupling of 1-N with ^{11}B is only observed for the tetrakis derivative **2** due to its tetrahedral symmetry [15]. Using a ^{15}N labeled derivative (from the Tp^{Me_2} ligand) we reported $^1J(^{205}\text{Tl},^{15}\text{N})$ of 714 Hz (DMSO- d_6) to 821 Hz (CDCl_3) [5]. In the present case, the coupling constant was observed only in the solid state, where there are no N–Tl bond breaking processes. The values are comprised between 668 Hz (**6**) and 835 Hz (**4**). In the case of compound **2**, the signal of 2-N is a multiplet, probably due to couplings with other thallium atoms in the solid.

The X-ray structures of most compounds under study have been determined (Z' is the number of independent molecules). It is interesting to see if there is a relationship between the crystal structures (see Scheme 1) and

Table 3
 ^{15}N NMR data (δ in ppm, J in Hz) of scorpionates **1–6**

Comp.	Tris/tetrakis	Subs.	Solvent	Pyrazole	
				Pos. 1	Pos. 2
1	Tris	Cpr	CDCl_3	–151.3	N.o.
			DMSO- d_6	–150.1	–74.6
			Solid	–149.0	–77.2
				$^1J(^{15}\text{N},^{205}\text{Tl}) = 806$	
2	Tetrakis	Cpr	CDCl_3	–157.0	N.o.
			DMSO- d_6	–155.1	–71.8
			Solid	–152.8	–68.2 ^a
				$^1J(^{15}\text{N},^{11}\text{B}) = 35.1$	
				$^1J(^{15}\text{N},^{11}\text{B}) = 35.3$	
3	Tris	Cbu	CDCl_3	–151.3	N.o.
			Solid	–150.8	–71.9
4	Tris	Cpe	CDCl_3	–151.1	N.o.
			Solid	–147.5	–72.6
5	Tris	Cy	CDCl_3	–151.5	N.o.
			DMSO- d_6	–150.4	N.o.
			Solid	–148.9	–72.5
				$^1J(^{15}\text{N},^{205}\text{Tl}) = 780$	
6	Tris	Cy,4Br	CDCl_3	–153.9	N.o.
			DMSO- d_6	–148.8	N.o.
			Solid	–151.4	–71.8
				$^1J(^{15}\text{N},^{205}\text{Tl}) = 668$	

^a Multiplet.

the NMR results in the solid state, particularly those of Table 2.

- [Tl(Tp^{Cpr})]₄ (**1**) This compound crystallizes in a very unusual structure. The four thallium atoms form a regular tetrahedron, each Tl being linked to the three N atoms of the scorpionate, Tl–Tl distance 3.647 Å [7,8]. The observation of two signals for 4-C only one of them coupled (282 Hz) may correspond to different conformations of the pyrazolyl residues in the ligand.
- [Tl(pz⁰Tp^{Cpr})] (**2**) Structure unknown. Four signals for 4-C only one of them coupled (263 Hz). One group of signals should belong to the pyrazolyl group not linked to thallium (the pz⁰), probably the most different (160.4, 105.4 and 138.0–139.3 ppm). The tetrakis thallium salt **2** could not be crystallized for X-ray structure determination. It gave very fibrous solids. It may be a polymer with Tl coordinated between several ligands with probably three or more different molecules in the solid.
- [Tl(Tp^{Cbu})] (**3**) Monomer, one independent molecule in the asymmetric unit [9]. Geometry: 4-C···Tl = 4.147 Å, 4-H···Tl = 3.580 Å, angle 4-C···4-H···Tl = 120.8°. Only one 4-C signal (233 Hz).
- [Tl(Tp^{Cpe})] (**4**) Monomer, three independent molecules in the asymmetric unit with slightly different orientations [9]. Geometry: 4-C···Tl = 4.143 Å, 4-H···Tl = 3.342 Å, angle 4-C···4-H···Tl = 144.4°; 4-C···Tl = 4.514 Å, 4-H···Tl = 3.911 Å, angle 4-C···4-H···Tl = 124.8°, 4-C···Tl = 3.849 Å, 4-H···Tl = 3.141 Å, angle 4-C···4-H···Tl = 133.5°. The different signals for 4-C only one of them coupled (194 Hz), may be corresponding to the shortest 4-C···Tl distance (3.849 Å).
- [Tl(Tp^{Cy})] (**5**) Monomer, no hydrogen interaction corresponding to 4-C···Tl interactions [10,11]. Two signals for 4-C none of them coupled.
- [Tl(Tp^{Cy,4Br})] (**6**) Monomer [11], the presence of a 4-bromo substituent prevents the 4-C···Tl interactions. Three signals for 4-C none of them coupled.

4. Conclusion

Although the NMR properties of scorpionates in solution have been reported in many publications, solid state studies are still uncommon. However, important information is lost in solution due to dynamic processes including fluxionality. In the case of thallium scorpionates **1–6** several interesting coupling constants involv-

ing ¹¹B and ²⁰⁵Tl have been determined. A very large ²⁰⁵Tl–¹³C coupling has been observed and assigned to a coupling between adjacent molecules in the crystal. An attempt has been made to correlate this coupling with the structures determined by X-ray crystallography.

Acknowledgements

Financial support was provided by the Spanish DGI/MCYT (Project no. BQU2000-0252). Dr. Jim Golen (University of Delaware) has been very helpful in discussing the crystallographic results. We thank Professor Julius Glaser (KTH, Sweden) for recording the ²⁰⁵Tl NMR spectrum of **2** in CDCl₃.

References

- [1] S. Trofimenko, Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligand, Imperial College Press, London, 1999.
- [2] C. Janiak, *Coord. Chem. Rev.* 163 (1997) 107.
- [3] C. Janiak, *Main Group Metal Chem.* 21 (1998) 33.
- [4] C. López, D. Sanz, R.M. Claramunt, S. Trofimenko, J. Elguero, *J. Organomet. Chem.* 503 (1995) 265.
- [5] D. Sanz, R.M. Claramunt, J. Glaser, S. Trofimenko, J. Elguero, *Magn. Reson. Chem.* 34 (1996) 843.
- [6] P. Ghosh, P.J. Desrosiers, G. Parkin, *J. Am. Chem. Soc.* 120 (1998) 10416.
- [7] A.L. Rheingold, L.M. Liable-Sands, S. Trofimenko, *Chem. Commun.* (1997) 1691.
- [8] A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, I.A. Guzei, S. Trofimenko, *Inorg. Chem.* 36 (1997) 6261.
- [9] A.L. Rheingold, G.P.A. Yap, L.N. Zakharov, S. Trofimenko, *Eur. J. Inorg. Chem.* (2002) 2335.
- [10] A.L. Rheingold, B.S. Haggerty, S. Trofimenko, *Angew. Chem. Int. Ed.* 33 (1994) 1983.
- [11] S. Trofimenko, A.L. Rheingold, L.M. Liable-Sands, *Inorg. Chem.* 41 (2002) 1889.
- [12] S. Braun, H.-O. Kalinowski, S. Berger, 150 and more Basic NMR Experiments, Wiley-VCH, Weinheim, 1998.
- [13] R.M. Claramunt, D. Sanz, M.D. Santa María, J.A. Jiménez, M.L. Jimeno, J. Elguero, *Heterocycles* 47 (1998) 301.
- [14] S. Trofimenko, *J. Am. Chem. Soc.* 89 (1967) 3170.
- [15] C. López, R.M. Claramunt, D. Sanz, C. Foces-Foces, F.H. Cano, R. Faure, E. Cayón, J. Elguero, *Inorg. Chim. Acta* 176 (1990) 195.
- [16] J. Glaser, personal communication.
- [17] C. López, D. Sanz, R.M. Claramunt, M.D. Santa María, J. Elguero, unpublished results.
- [18] H. Schumann, C. Janiak, H. Khani, *J. Organomet. Chem.* 330 (1987) 347.
- [19] H. Schumann, C. Janiak, M.A. Khan, J.J. Zuckerman, *J. Organomet. Chem.* 354 (1988) 7.
- [20] H. Takemura, S. Nakashima, N. Kon, M. Yasutake, T. Shimoyozu, T. Inazu, *J. Am. Chem. Soc.* 123 (2001) 9293.
- [21] E. Craven, E. Mutlu, D. Lundberg, S. Temizdemir, S. Dechert, H. Brombacher, C. Janiak, *Polyhedron* 21 (2002) 553.