

Metal polypyrazolylborates
XIV. Organomercury(II) complexes with
hydridotris(3,5-diphenyl-1 *H*-pyrazolyl) borate and
hydridotris(4-bromo-1 *H*-pyrazolyl) borate. The X-ray crystal structure of
[HB(3,5-Ph₂pz)₃]HgC₂H₅

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Abstract

The preparation and characterisation of R–Hg⁺ ion (R = Me, Et, Pr, *i*-Pr, Ph, *p*-Tol, Benzyl, 5-Me-Thienyl, or Ferrocenyl) complexes with the ligands Tp^{Ph₂} (hydridotris(3,5-diphenyl-1 *H*-pyrazol-1-yl)borato) or Tp^{4Br} (hydridotris(4-bromo-1 *H*-pyrazol-1-yl)borato) are here reported. Comparison from ¹H, ¹³C, and ¹⁹⁹Hg NMR spectra show the ligand Tp^{Ph₂} to be a better overall donor than the Tp^{4Br} one. The X-ray crystal structure of the complex Et–Hg · Tp^{Ph₂}, which is here reported, represents the first case in which the Hg (bonded to an organic R-group and a tripodal *N*-donor ligand) is tetrahedrally coordinated (with some distortions), instead of being T-shaped. The compound is orthorhombic, space group *P* 2₁2₁2₁ with *a* = 12.966(3) Å, *b* = 16.940(3) Å, and *c* = 18.412(4) Å; *V* = 4044(1) Å³; *Z* = 4; *R*(*R_w*) = 0.056(0.057). © 1998 Elsevier Science S.A.

Keywords: Mercury(II) complexes; Pyrazolylborates; ¹⁹⁹Hg; Tetrahedral coordination

1. Introduction

The chemistry of organomercury complexes with variously substituted polypyrazolylborates (or related ligands) has been much investigated since the pioneering works by Canty et al. [1–5]. Much attention [6–9] has been focused on the singular behaviour of the complexed mercury atom, as regards the dependence of coordination numbers and the geometry of the metal centre on the nature of both the mercury species and the ligands. An earlier work established a substantially tetrahedral structure in solution of X–Hg · Tp^{*}, where X is a halogen or *pseudo*-halogen [10,11]. Concerning the organomercury polypyrazolylborates, the coordinative situation at the metal centre is regularly described as a typical one as follows: one strong Hg–C bond, one

strong Hg–N bond nearly colinear, and another (or two other) weaker and longer Hg–N one(s). Often such situations have been reported as T-shaped geometries, in that the longer Hg–N bond makes angles of ca. 90° with the main C–Hg–N axis [12,13]. Such behaviour may be regarded as an aspect of the well-known tendency of Hg to avoid, whenever possible, coordination numbers greater than two [14,15]. This is a consequence of high promotion energies needed to involve further 6*p* orbital contribution to the Hg hybridisation scheme [16]. At variance with the 'inorganic' mercury moieties, tetrahedral organomercury pyrazolylborates are virtually unknown. Indeed, the species containing the R(Ar)–Hg⁺ moiety show solid structure more similar to a T-shaped coordination scheme than a tetrahedral one [1,17,18] and, anyway, have been shown to be essentially 2-coordinated and fluxional in solution [1,17,18]. In addition, also the species featuring the moiety R(Ar)–S–Hg⁺ behave in a similar manner [18–20]. Here, the structure

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of the $\text{Et-Hg} \cdot \text{Tp}^{\text{Ph}_2}$ is reported which show for the first time a substantially tetrahedral Hg centre in the solid state. This is perhaps a striking feature probably due to the peculiar donor properties and steric demand of the ligand. Such a feature is also of interest in that coordination numbers greater than two are of particular biological significance as in the situation involved in the Hg–MerR biosensor [21–23]. Moreover, enhancing the coordination number of organomercury(II) appears to be a remarkable requirement in the activation of the Hg–C bond cleavage reaction, in both the bacterial degradation [24] and other reactions such as the symmetrization of arylmercury(II) salts [25–27].

2. Results and discussion

The compounds are prepared from the interaction of KTp^{Ph_2} or $\text{KTp}^{4\text{Br}}$ and the appropriate alkyl- or arylmercury chlorides in water or dichloromethane medium, according to the solubility, in order to minimise the well-known Hg reduction by trispyrazolylborato ligands [10,11,17–20]. The metathetic reaction proceeds smoothly to afford the complexes which are sufficiently air-stable solids, but not quite so in solution. Like other mercury trispyrazolylborates, they also are prone to the typical decomposition which leads to metallic Hg deposition on standing [17–20,28]. In this respect, the $\text{Tp}^{4\text{Br}}$ derivatives show a quicker decomposition than the Tp^{Ph_2} ones, except perhaps for the cyanomercury derivatives, in which case the solution stability order is reversed. However, all these complexes are even less stable than the corresponding Tp^* derivatives [17,18]. Indeed, not all the complexes $\text{R-Hg} \cdot \text{Tp}^{4\text{Br}}$ corresponding to the $\text{R-Hg} \cdot \text{Tp}^{\text{Ph}_2}$ can be prepared in comparable conditions. The complexes have been characterised through spectroscopic techniques such as the IR spectroscopy, ^1H , ^{13}C , and ^{199}Hg NMR. Conductivity data together with some molecular weight determinations show the complexes to be undissociated and monomeric in solution. This is in line with their supposed nature of internal, neutral complexes.

The infrared spectra show several bands expected for the ligand moieties; the ‘ring breathing’ bands appear at 1540–1545, and 1509–1515 cm^{-1} , and the characteristic B–H absorption bands appearing at 2589–2624, and 2460–2467 cm^{-1} , the C–H stretching vibrations due to the pyrazole ring are seen at 3040–3057 and 3070–3135 cm^{-1} for Tp^{Ph_2} and $\text{Tp}^{4\text{Br}}$, respectively.

The ^1H NMR spectra for the Tp^{Ph_2} complexes which are obviously complicated by the presence of two Ph-groups per pyrazole ring, can be described as follows. The *ortho*- and *meta*-protons in such groups appear as overlapping multiplets falling in the range of (6.86–7.50), as do the *para* ones, which instead are seen in the interval (7.63–7.96). The H-4 protons are singlets with-

out any satellite peaks and are slightly shifted downfield with respect to their resonance position in the K salt of the ligand. This accounts for an overall net flow charge from the ligand to mercury and is also true for the complexes from the other ligand, and moreover, the same qualitative effect has been recognised previously for other ligands [17–20]. The spectra of the complexes show the H-3 and H-5 as singlets for the ligand moiety, and the expected signals from the R group linked to Hg. Comparing analogous complexes from either $\text{Tp}^{4\text{Br}}$ or Tp^{Ph_2} it may be noted that the R-groups in the former feature a general downfield shift with respect to those from Tp^* [19], while the reverse is true for the latter. This reasonably indicates that $\text{Tp}^{4\text{Br}}$ is a poorer donor than Tp^* (which seems likely in view of the presence of the Br in the pz-rings, and in line with the more rapid deboronation of the resulting complexes). Another account of the upfield shift in Tp^{Ph_2} derivatives is possibly linked to a particular mean alignment of the three 3-Ph groups in the Tp^{Ph_2} ligand towards the (Hg–)R group. Indeed, if such an alignment is more in a ‘facial’ than ‘edge’ fashion, as suggested by the crystal structure, then the nuclei in the R group should be over-shielded.

The $\nu(\text{Hg-C})$ stretching frequencies may be considered an independent assessment of the greater donor power of the ligand Tp^{Ph_2} , while those relevant to $\text{R-Hg} \cdot \text{Tp}^{\text{Ph}_2}$, ranging from 560 to 571 cm^{-1} (for comparison, the Tp^* ones are 510–540 cm^{-1}), and the ones relevant to $\text{Tp}^{4\text{Br}}$, are distinctly higher, clustering near 610 cm^{-1} . This is consistent with a reinforcement of the C–Hg bond when the Hg–N one becomes weaker as a result of lower donating power of the ligand.

As regards the ^{199}Hg chemical shift, the values for Tp^{Ph_2} complexes are higher (less negative) than the corresponding $\text{Tp}^{4\text{Br}}$ ones. Fig. 1 shows the trends of ^{199}Hg chemical shift for complexes featuring simple

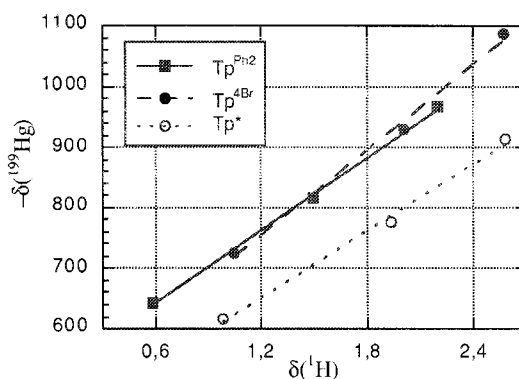


Fig. 1. Trends of ^{199}Hg chemical shift for the Me–Hg, Et–Hg, and *i*-Pr–Hg complexes from the ligands Tp^{Ph_2} , $\text{Tp}^{4\text{Br}}$, and Tp^* as a function of ^1H chemical shift. The lines from linear regression are, respectively, as follows: $y_1 = 523.63 + 199.32x$; $R = 0.99933$; $y_2 = 487.01 + 228.11x$; $R = 0.99409$; $y_3 = 430.04 + 184.70x$; $R = 0.99738$.

R–Hg groups (Me, Et, and *i*-Pr) as a function of their respective ^1H chemical shift values. As may be seen, in each case there is a good correlation. This reasonably implies that, except for bulkier R–Hg groups, the donor power of the ligands follows the order $\text{Tp}^* > \text{Tp}^{\text{Ph}_2} > \text{Tp}^{4\text{Br}}$, in agreement with the results of a previous work in which a series of cyanomercury poly(pyrazolyl) borates was examined [11]. In this connection, the ^{199}Hg results seem consistently to indicate that the chemical shift increases with increasing donor power of the ligand. Although the present ligands are not part of that series, an extrapolation of the trend would indicate that the Tp^{Ph_2} ligand is a better donor than $\text{Tp}^{4\text{Br}}$.

The ^{13}C spectra of the complexes show the peaks expected for such type of complexes. In particular, the Ph groups of Tp^{Ph_2} could be assigned for all the complexes except those bearing some other Hg-bonded aryl group (Fc, MeTf) and partly the *i*-Pr one. As previously reported [19], the carbon atom directly bonded to Hg (except the case of methyl), are generally not observed. Repeated efforts to detect them at low temperature (up to -60) have failed to show any significant change in the spectra, as it previously happened with other organomercury pyrazolylborates. This, and the absence of any coupling satellite peaks between Hg or R(Hg) and the pyrazole rings stands against a rigid structure of such complexes in solution, favouring instead a fluxional model, similar to that observed for the corresponding complexes with other pyrazolylborato ligands.

In agreement with findings about the chemical shifts exhibited by these groups in the protonic spectra, Me is seen at -2.16 ppm for the ligand Tp^{Ph_2} , $+16.2$ ppm for $\text{Tp}^{4\text{Br}}$, while that for Tp^* falls at -7.2 ppm. Analogous, even if less pronounced, is the behaviour of the Et group (because of this group only the $\beta\text{-CH}_3$ is seen): 15.2, 15.4, and 10.0 ppm, respectively. This is further evidence supporting the given order of donating power of the ligands.

2.1. X-ray crystal structure of (hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato ethylmercury

A perspective view of the molecule is shown in Fig. 2, and the most relevant bond distances and angles and a summary of crystallographic data are presented in Tables 1 and 2.

The Tp^{Ph_2} moiety acts as a tripodal ligand forming a triple –N–N– bridge between Hg and B atoms. The mercury (II) atom is tetracoordinated in a tetrahedral arrangement, which, although highly distorted, saves a fair symmetry, whereas the boron atom displays an exactly tetrahedral configuration.

In the literature, only few X-ray structures are reported in which Hg(II) is tetracoordinated in a tetrahedral arrangement. The most regular are those found in

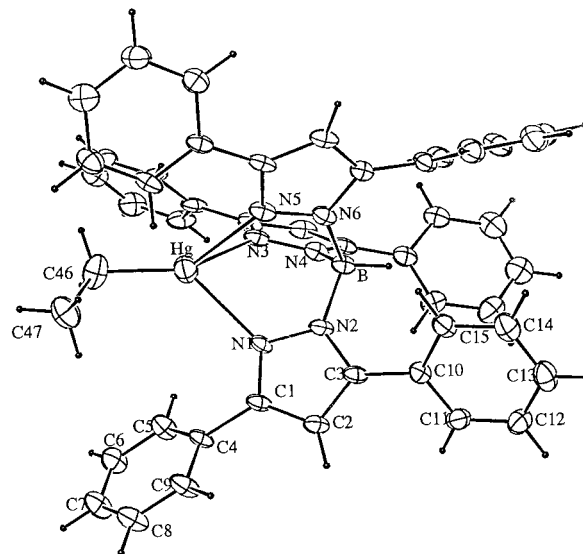


Fig. 2. Ortep view of (hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato ethylmercury. For clarity's sake, only a part of the atoms of complex is labelled.

the complex cations composed of the tripodal ligand np_3 [$= \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$] and XHg [$\text{X} = \text{I}, \text{Me}, \text{S}(p\text{-CH}_3\text{C}_6\text{H}_4)$], where the metal atom is coordinated to three phosphorous atoms [29,30].

In other cases, complexes of alkyl-Hg(II) cations, where the mercury atom is tri- or tetra-coordinated to N-donors ligands show, usually, a dominant, almost linear, strong Hg–N bond with lengths in the range 2.12–2.28 Å, and one or two more weak Hg–N bonds with lengths in the range 2.43–2.96 Å (see Refs. [4,29–31] and references therein).

In the title complex, otherwise, the three Hg–N bonds, although significantly not equivalent, are, however, not so different. In particular, their lengths [2.36(1), 2.40(1) and 2.50(1) Å] fall between the above-mentioned ranges, suggesting that these bonds can be classified as bonds of medium strength.

Table 1

Selected bond lengths (Å) and valence angles (°) with their e.s.d.s in parentheses

Hg–N(1)	2.36(1)	Hg–N(3)	2.40(1)
Hg–N(5)	2.50(1)	Hg–C(46)	2.03(2)
B–N(2)	1.56(1)	B–N(4)	1.55(2)
B–N(6)	1.53(1)	N(1)–N(2)	1.36(1)
N(3)–N(4)	1.36(1)	N(5)–N(6)	1.38(1)
N(1)–Hg–N(3)	77.4(5)	N(1)–Hg–N(5)	82.5(5)
N(1)–Hg–C(46)	132.7(9)	N(3)–Hg–N(5)	77.5(5)
N(3)–Hg–C(46)	136.2(9)	N(5)–Hg–C(46)	129.1(9)
N(2)–B–N(4)	110(2)	N(2)–B–N(6)	110(2)
N(4)–B–N(6)	110(2)	Hg–N(1)–N(2)	118(1)
B–N(2)–N(1)	119(1)	Hg–N(3)–N(4)	119(1)
B–N(4)–N(3)	119(1)	Hg–N(5)–N(6)	115(1)
B–N(6)–N(5)	123(1)		

Table 2
Summary of crystallographic data

Crystal size (mm)	0.15×0.20×0.30
Formula	HgBN ₆ C ₄₇ H ₃₉
Fw	899.3
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	12.966(3)
<i>b</i> (Å)	16.940(3)
<i>c</i> (Å)	18.412(4)
<i>V</i> (Å ³)	4044(1)
<i>Z</i>	4
<i>F</i> (000)	1792
<i>D</i> _c (g cm ⁻³)	1.48
λ(Cu Kα) (Å)	1.54056
θ _{max} (°)	72
μ (cm ⁻¹)	76.2
No. of indep. refl.	4416
No. of refl. above 3σ(1)	3052
No. of refined parameters	496
Goodness of fit	0.942
<i>R</i>	0.056
<i>R</i> _w	0.057
<i>R</i> (inverted structure)	0.075
<i>R</i> _w (inverted structure)	0.078

The presence of the ethyl group, besides removing the potential three-fold symmetry around the Hg–*B* axis, is, also, a major factor responsible for the deviations from the ideal tetrahedral values of the valence angles at Hg, as shown by comparison with the analogous condition of the boron atom. These distortions are the result of a combination of intra- and intermolecular interactions. In fact, the direct effect of the steric hindrance of the ethyl group is the departure of the neighbouring phenyl groups, which, sharing in the crystal packing, induce distortions in the soft coordination sphere of Hg.

The phenyl and pyrazolyl rings are perfectly planar [maximum out of plane displacement less than 0.03(2) Å] and display bond lengths and angles in the expected

ranges and, moreover, a high correspondence in the conformational parameters. In fact, the three pyrazole rings form with the attached phenyl rings dihedral angles which are 36.5(4), 33.2(4), and 24.0(4)° on the Hg side, and 44.3(4), 45.0(4), and 49.0(4)° on the *B* side, while the dihedral angles between the phenyl rings linked to the same pyrazolyl fragment are 75.1(4), 76.1(4), and 71.6(4)°.

The C(46)–Hg bond length of 2.03(2) Å is typical of this bond in Hg(II) complexes containing nitrogen donor ligands (Refs. [31–33] and references therein).

In Table 3, the salient features of the crystal structures of the present complex together with some related ones are compared. The first two can be described as displaying a distorted tetrahedral environment around mercury, while the others are to be viewed as irregular geometries.

As can be seen, the longest Hg–N bond in NC–Hg·Tp* is anyway shorter than the shortest Hg–N distance in Et–Hg·Tp^{Ph₂}.

This is a clear indication that in the former the Hg atom is much more strongly bound than that in the latter. Furthermore, the distances of the Hg atom from the mean planes of the pyrazole rings in the former are considerably lower than the corresponding ones in the latter. The Hg–N bonds show a less regular behaviour in Et–Hg·Tp^{Ph₂} than in NC–Hg·Tp*, while the reverse is true for the C–Hg–N bond angles. These features reflect the fact that the cyanomercury cation is definitely a far stronger Lewis acid than organomercury ones and can be best compared with X–Hg⁺ cations (where X = halogen, nitrate, and similar inorganic anions). Another convincing proof of the tighter binding of NC–Hg⁺ cations with pyrazolylborato ligands with respect to alkylmercury cations comes from their solution structure. While the complexes from NC–Hg⁺ moieties show rigid tetracoordination [11], those from R(or Ar)–Hg⁺ ones are generally fluxional even at very low temperatures [1–5,19].

Table 3
Comparison of selected structural data for complexes with tridentate nitrogen donor ligands

^a	Et–Hg·Tp ^{Ph₂}	NC–Hg·Tp ^a	[Me–Hg·(py) ₃ COH]NO ₃	[Me–Hg·(py) ₂ (<i>N</i> -MeIm)COH]NO ₃
Hg–C (Å)	2.03(2)	2.01(2)	2.03(2)	2.05(1)
Hg–N(A) (Å)	2.36(1)	2.20(2)	2.28(1)	2.13(1)
C–Hg–N(A) (deg)	132.7(9)	142.1(8)	150(1)	170(0)
Hg···plane (Å)	–0.840(1)	–0.0716(8)	–0.054(1)	0.075(0)
Hg–N(B) (Å)	2.40(1)	2.26(1)	2.45(1)	2.66(1)
C–Hg–N(B) (deg)	136.2(9)	125.9(9)	132(1)	110(0)
Hg···plane (Å)	–0.661(1)	–0.0322(6)	0.349(1)	–0.612(0)
Hg–N(C) (Å)	2.50(1)	2.34(1)	2.53(1)	2.71(1)
C–Hg–N(C) (deg)	129.1(9)	120.6(6)	119(1)	114(0)
Hg···plane (Å)	–0.482(1)	0.2365(9)	0.590(1)	–1.136(0)
Reference	this work	[11]	[4]	[4]

^a The N(A)–N(C) are given according to increasing Hg–N distance.

The comparison of the present structure with the other two is less readily feasible and somewhat more complicated. Indeed, contrasting indications may be found. The Hg–N distances (2.36–2.50 Å) and the C–Hg–N angles (129.1–136.2°) are less spread than in the other cases {(2.28–2.53 and 2.13–2.71 Å) (119–150 and 110–170°)}. Furthermore, the angle at Hg with the strongest bound nitrogen atom (132.7(9)) is substantially lower (and closer to the tetrahedral value) than the value of 150(1) found in the complex [Me–Hg·(py)₃COH]NO₃ or 170(0) for the [Me–Hg·(py)₂(N-MeIm)COH]NO₃ one. The latter angles, conversely, are closer to the typical value of T-shaped geometries.

This should suggest more symmetry in the present complex binding scheme, i.e., the tendency of concentrating high electron densities in two collinear bonds is better avoided here than in the other two cases.

Nevertheless, the average distance from the mean planes which is here nearly double than that in the complex [Me–Hg·(py)₃COH]NO₃ has been reasonably taken as an indication of a tighter binding of the mercury atom in the latter.

3. Experimental

3.1. General comments

Concentration was always carried out in vacuo (water aspirator). The samples were dried in vacuo till constant weight (20°C, ca. 0.1 Torr). Carbon, hydrogen, and nitrogen analyses were carried out on a Fisons Instruments EA 1108 CHNS-O, while molecular weight determinations were performed by a Knauer vapor osmometer. Infrared spectra were recorded from 4000 to 250 cm⁻¹ on a Perkin-Elmer 2000 System Series FTIR instrument. ¹H, ¹³C and ¹⁹⁹Hg NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (299.94 MHz for ¹H, 75.05 MHz for ¹³C, and 53.36 MHz for ¹⁹⁹Hg). Some spectra were also recorded on a Varian Gemini-200 (200 MHz for ¹H, 50 MHz for ¹³C). The chemical shift is reported in ppm from Me₄Si (¹H and ¹³C, calibration from internal deuterium solvent lock) values. The conductivity of the acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

3.2. Syntheses

The salt HgCl₂ was of reagent grade (Aldrich). All other starting organomercury chlorides, except methyl mercury chloride (Strem Chem.), were prepared from HgCl₂ and the appropriate Grignard reagent according to the standard method [34]. Ferrocenylmercury chloride was obtained according to Ref. [35]. The 4-bromopyrazole was commercially available (Aldrich) and was used

as received; 3,5-diphenylpyrazole was prepared by a published procedure [22] which is found very satisfactory.

3.2.1. Ligands

3.2.1.1. Potassium [hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] (KTp^{Ph₂}). This was prepared through a procedure similar to that of Ref. [22], except for washing with hot hexane and recrystallisation from diethyl ether. The mixture of 3,5-diphenylpyrazole (50 g, 0.227 mol) with KBH₄ (3.067 g, 0.057 mol) was eventually heated at 275°C until 3 equiv. of hydrogen per KBH₄ had evolved. Yield: 30.68 g. (76%); m.p. 271–273°C. (Found: C, 75.83; H, 5.01, N, 11.76. Calcd. for K[C₄₅H₃₄N₆B]: C, 76.26; H, 4.84; N, 11.86). NMR: ¹H(CDCl₃) δ[6.94–7.30 m (18H), 7.83–7.94 m (12H), (m, Ph-3 or Ph-5)], 6.78 (s, H-4); ¹³C (CDCl₃) δ 152.0, 151.6 (C-3 or C-5), 103.8 (C-4); 136.7, 135.2 (C-*ipso*), 128.5, 126.5 (C-*ortho*), 129.9, 129.5 (C-*meta*), 127.9, 127.5 (C-*para*) (Ph-3 or Ph-5); IR: 3039w ν(C–H), 2527w ν(B–H), 1544m (ring breathing).

3.2.1.2. Potassium [hydridotris(4-bromo-1H-pyrazol-1-yl)borato] (KTp^{4Br}). The ligand was prepared as already described [36]. Yield: 12.72 g. (77%); m.p. 287–289°C. (Found: C, 22.22; H, 1.54, N, 16.93. Calcd. for K[C₉H₇N₆BBr₃): C, 22.11; H, 1.44; N, 17.19). NMR: ¹H (CD₃OD) δ 7.30, 7.59 (s, H-3 or H-5); ¹³C (CD₃OD) δ 142.8, 136.6 (C-3 or C-5), 93.9 (C-4); IR: 3137m, 3096m ν(C–H), 2420vs ν(B–H), 1511m (ring breathing).

3.2.2. Complexes

An aqueous solution of organylmercury(II) chloride (1 mmol) and an aqueous solution of potassium [hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] (KTp^{Ph₂}) or potassium [hydridotris(4-bromo-1H-pyrazol-1-yl)borato] (KTp^{4Br}) (1 mmol) were mixed at room temperature; the colourless precipitates which formed immediately in the cases of **1–4** and **10–14** were washed in H₂O.

Compounds **5–9** were prepared by mixing of a dichloromethane solution (30 ml) of arylmercury(II) chloride (1 mmol) with a suspension of KTp^{Ph₂} (1 mmol) in dichloromethane (30 ml). The resulting suspension was stirred for 10'–40' and then filtered to separate the formed KCl. The filtered solution was evaporated to dryness; the residue was purified from dichloromethane–Et₂O.

Compound **15**, Cyanomercury [hydridotris(4-bromo-1H-pyrazol-1-yl)borato] could be satisfactorily prepared by mixing a methanol solution of Hg(CN)₂ (1 mmol) with a solution of KTp^{4Br} in methanol (1 mmol). A colourless precipitate is obtained after a few minutes

under stirring. This was washed in MeOH–H₂O (1:3 v/v) to remove the KCl that formed.

3.2.2.1. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] methylmercury

Compound 1, (Tp^{Ph₂}–Hg–CH₃). Yield: 593 mg (67%); m.p.: 240–242°C; M.W. (Found/Calcd.) 862/884.7 (Found: C, 62.57, H, 4.46, N, 9.70. Calcd. for C₄₆H₃₇N₆BHg C, 62.45; H, 4.22; N, 9.50). NMR: ¹H (CDCl₃): δ 6.86–7.42 (24 H), 7.50–7.82 (6H) (m, Ph-3 or Ph-5) 6.52 (s, H-4), 0.58 (|²J| = 243 Hz, Me); ¹³C (CDCl₃) δ 152.8, 150.9 (C-3 or C-5), 105.1 (C-4); 133.2, 132.2 (C-*ipso*), 128.1, 125.6 (C-*ortho*), 129.7, 128.4 (C-*meta*), 127.7, 127.5 (C-*para*) (Ph-3 or Ph-5); –2.16 (Me); ¹⁹⁹Hg NMR (δ) –642.4; IR: 3040w ν(C–H), 2589w ν(B–H), 1542w (ring breathing), 571s ν(Hg–C).

3.2.2.2. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] ethylmercury

Compound 2, (TP^{Ph₂}–Hg–C₂H₅). Yield: 638 mg (71%); m.p.: 237–239°C; M.W. (Found/Calcd.) 850/898.7 (Found: C, 63.08, H, 4.62, N, 9.65. Calcd. for C₄₇H₃₉N₆BHg C, 62.81; H, 4.37; N, 9.35). NMR: ¹H (CDCl₃): δ 6.92–7.49 (24 H), 7.68–7.80 (6H) (m, Ph-3 or Ph-5), 6.51 (s, H-4), 0.82, 1.50 (|²J| = not observed, |³J| = not observed, Et); ¹³C (CDCl₃) δ 152.7, 150.9 (C-3 or C-5), 105.1 (C-4); 133.6, 132.2 (C-*ipso*), 128.3, 125.5 (C-*ortho*), 129.7, 128.5 (C-*meta*), 127.9, 127.5 (C-*para*) (Ph-3 or Ph-5); [15.2 (CH₃), not observed (CH₂), (Et)]; ¹⁹⁹Hg NMR (δ) –815.3; IR: 3056w ν(C–H), 2583w ν(B–H), 1540w (ring breathing), 564s ν(Hg–C).

3.2.2.3. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] propylmercury

Compound 3, (Tp^{Ph₂}–Hg–Pr). Yield: 575 mg (63%); m.p.: 229–231°C; M.W. (Found/Calcd.) 901/912.7 (Found: C, 62.65, H, 4.60; N, 9.03. Calcd. for C₄₈H₄₁N₆BHg C, 63.17; H, 4.53; N, 9.21). NMR: ¹H (CDCl₃): δ 6.87–7.51 (24 H), 7.69–7.74 (6H) (m, Ph-3 or Ph-5), 6.52 (s, H-4); 0.44, 1.10, 1.51 (|²J| = 246 Hz, Pr); ¹³C (CDCl₃) δ 152.8, 150.9 (C-3 or C-5), 105.2 (C-4); 133.6, 132.2 (C-*ipso*), 128.3, 125.6 (C-*ortho*), 129.6, 128.9 (C-*meta*), 127.8, 127.5 (C-*para*) (Ph-3 or Ph-5); [26.1 (CH₃), not observed (CH₂–CH₂), (Pr)]; ¹⁹⁹Hg NMR (δ) –810.3; IR: 3053w ν(C–H), 2624w ν(B–H), 1540m (ring breathing), 568s ν(Hg–C).

3.2.2.4. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] isopropylmercury

Compound 4, (Tp^{Ph₂}–Hg–i-Pr). Yield: 529 mg (58%); m.p.: 242–244°C; (Found: C, 62.93; H, 4.71; N, 9.30. Calcd. for C₄₈H₄₁N₆BHg C, 63.17; H, 4.53; N, 9.21). NMR: ¹H (CDCl₃): δ 6.96–7.50 (24 H), 7.68–7.94 (6H) (m, Ph-3 or Ph-5), 6.57 (s, H-4); 1.46, 2.20,

(i-Pr); ¹³C (CDCl₃) δ 153.7, 151.6 (C-3 or C-5), 105.8 (C-4); 131.9, (C-*ipso*), 129.5–125.6 (C-*ortho*, C-*meta*, C-*para*) (Ph-3 or Ph-5); [23.8 (CH₃), not observed (CH), (i-Pr)]; ¹⁹⁹Hg NMR (δ) –966.3; IR: 3056w ν(C–H), 2624w ν(B–H), 1541m (ring breathing), 567m ν(Hg–C).

3.2.2.5. Hydridotris(3,5-diphenyl-1H R-pyrazol-1-yl)borato] phenylmercury

Compound 5, (Tp^{Ph₂}–Hg–Ph). Yield: 814 mg (86%); m.p.: 181–183; M.W. (Found/Calcd.) 898/946.7 (Found: C, 65.19; H, 4.38; N, 8.84. Calcd. for C₅₁H₃₉N₆BHg C, 64.66; H, 4.15; N, 8.87). NMR: ¹H (CDCl₃): δ 6.93–7.48 (29 H), 7.67–7.77 (6H) (m, Ph-3 or Ph-5 and Ph–Hg), 6.56 (s, H-4); ¹³C (CDCl₃) δ 153.2, 151.2 (C-3 or C-5), 105.3 (C-4); 132.9, 132.1 (C-*ipso*), 128.0, 125.6 (C-*ortho*), 129.7, 128.5 (C-*meta*), 127.6, 127.4 (C-*para*) (Ph-3 or Ph-5); [138.3, 128.9, 128.3, 127.7 (Ph)]; ¹⁹⁹Hg NMR (δ) –993.8; Ir: 3060w ν(C–H), 2617w ν(B–H), 1540w (ring breathing), 560m ν(Hg–C).

3.2.2.6. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] p-tolylmercury

Compound 6, (Tp^{Ph₂}–Hg–p-tolyl). Yield: 740 mg (77%); m.p.: 190°C melts with charring; (Found: C, 64.42; H, 4.45; N, 8.82. Calcd. for C₅₂H₄₁N₆BHg C, 65.01; H, 4.30; N, 8.75). NMR: ¹H (CDCl₃): δ 6.92–7.44 (28 H), 7.63–7.78 (6H) (m, Ph-3 or Ph-5 and p-Tolyl), 6.55 (s, H-4), 2.38 (Me–p-Tolyl); ¹³C (CDCl₃) δ 153.7, 151.6 (C-3 or C-5), 105.8 (C-4); 132.6, 131.9 (C-*ipso*), 128.6, 126.1 (C-*ortho*), 130.2, 129.4 (C-*meta*), 128.2, 128.0 (C-*para*) (Ph-3 or Ph-5); [137.8, 128.5, 126.3, 127.7 (p-Tolyl), 21.7 (CH₃ of p-Tolyl)]; IR: 3059w ν(C–H), 2606w ν(B–H), 1543w (ring breathing), 565s ν(Hg–C).

3.2.2.7. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] benzylmercury

Compound 7, (Tp^{Ph₂}–Hg–Bz). Yield: 673 mg (70%); m.p.: 175°C melts with charring; (Found: C, 64.60; H, 4.34, N, 8.32. Calcd. for C₅₂H₄₁N₆BHg C, 65.01; H, 4.30; N, 8.75). NMR: ¹H (CDCl₃): δ 6.96–7.50 (29 H), 7.63–7.91 (6H) (m, Ph-3 or Ph-5 and benzyl), 6.55 (s, H-4), 3.26 [CH₂ (benzyl)]; ¹³C (CDCl₃) δ 153.0, 151.0 (C-3 or C-5), 105.3 (C-4); 133.4, 132.1 (C-*ipso*), 128.6, 125.6 (C-*ortho*), 129.7, 129.4 (C-*meta*), 127.9, 127.7 (C-*para*) (Ph-3 or Ph-5); [131.2, 128.9, 128.0, 127.5 (benzyl), not observed CH₂ (benzyl)]; ¹⁹⁹Hg NMR (δ) –1104.6; IR: 3057w ν(C–H), 2595w ν(B–H), 1541w (ring breathing), 568s ν(Hg–C).

3.2.2.8. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato] (5-methyl)thienylmercury

Compound 8, (Tp^{Ph₂}–Hg–MeTf). Yield: 725 mg (75%); m.p.: 168–170°C; (Found: C, 61.41, H, 4.23; N,

8.65. Calcd. for $C_{50}H_{39}N_6BHgS$: C, 62.12; H, 4.07; N, 8.69. NMR: 1H ($CDCl_3$): δ 6.99–7.47 (24 H), 7.55–7.78 (6H) (m, Ph-3 or Ph-5), 6.56 (s, H-4), [7.01 d, 7.04 d (Tf), 2.58 CH_3 -Tf]; ^{13}C ($CDCl_3$) δ 153.9, 151.7 (C-3 or C-5), 105.9 (C-4), [130.3–126.1 (C-*ipso*, C-*ortho*, C-*meta*, C-*para*) (Ph-3 or Ph-5)]; [134.9, 132.5, 127.9, 125.5 (thiophene), 15.6 CH_3 (thiophene)]; ^{199}Hg NMR (δ) –856.5; IR: 3061w ν (C–H), 2604w ν (B–H), 1544m (ring breathing), 566s ν (Hg–C).

3.2.2.9. Hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato]mercuryferrocene

Compound 9, (TP^{Ph_2} -Hg-Fc). Yield: 927 mg (88%); m.p.: 150–152°C. (Found: C, 62.21, H, 4.16; N, 7.98. Calcd. for $C_{55}H_{43}N_6BFeHg$: C, 62.68; H, 4.11; N, 7.97). NMR: 1H ($CDCl_3$): δ 6.98–7.46 (24 H), 7.82–7.91 (6H) (m, Ph-3 or Ph-5), 6.57 (s, H-4), [4.45–4.51 m, 4.23 br, 4.26 br, 4.08–4.13 m (Fc)]; ^{13}C ($CDCl_3$) δ 153.3, 151.1 (C-3 or C-5), 105.5 (C-4), [131.4–125.6 (C-*ipso*, C-*ortho*, C-*meta*, C-*para*) (Ph-3 or Ph-5)]; [74.7, 72.6, 70.0, 69.6, 67.9 (ferrocene)]; ^{199}Hg NMR (δ) –738.9; IR: 3057w ν (C–H), 2610w ν (B–H), 1542m (ring breathing), 567s ν (Hg–C).

3.2.2.10. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]methylmercury

Compound 10, (TP^{4Br} -Hg- CH_3). Yield: 572 mg (86%); m.p. 93–95°C. M.W. (Found/Calcd.) 660/664.7 (Found: C, 17.98; H, 1.64; N, 12.42. Calcd. for $C_{10}H_{10}N_6BBr_3Hg$: C, 18.07; H, 1.52; N, 12.64). NMR: 1H ($CDCl_3$) δ 7.71, 7.50 (s, H-3 or H-5), 1.04 ($|^2J| = 233$ Hz, Me); ^{13}C ($CDCl_3$) δ 140.9, 136.0 (C-3 or C-5), 93.0 (C-4), 16.2 (Me); ^{199}Hg NMR (δ) –732.3; IR: 3066w ν (C–H), 2480w ν (B–H), 1510w (ring breathing), 611s ν (Hg–C).

3.2.2.11. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]ethylmercury

Compound 11, (TP^{4Br} -Hg- C_2H_5). Yield: 563 mg (83%); m.p. 81–83°C. M.W. (Found/Calcd.) 661/678.8 (Found: C, 20.10; H, 1.93; N, 12.79. Calcd. for $C_{11}H_{12}N_6BBr_3Hg$: C, 19.47; H, 1.78; N, 12.38). NMR: 1H ($CDCl_3$) δ 7.72, 7.52 (s, H-3 or H-5), [1.45, 2.01 ($|^2J| = 210$ Hz, $|^3J| = 302$ Hz, Et)]; ^{13}C ($CDCl_3$) δ 141.5, 136.6 (C-3 or C-5), 93.1 (C-4), [15.4 (CH_3), not observed (CH_2), (Et)]; ^{199}Hg NMR (δ) –923.5; IR: 3070w ν (C–H), 2466w ν (B–H), 1512w (ring breathing), 610s ν (Hg–C).

3.2.2.12. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]n-propylmercury

Compound 12, (TP^{4Br} -Hg-Pr). Yield: 513 mg (74%); m.p. 79–82°C. (Found: C, 20.88, H, 2.10; N, 12.02. Calcd. for $C_{12}H_{14}N_6BBr_3Hg$: C, 20.80; H, 2.04; N, 12.13). NMR: 1H ($CDCl_3$) δ 7.71, 7.48 (s, H-3 or H-5), [1.09, 1.82, 2.07 ($|^2J| = 221$ Hz, Pr); ^{13}C ($CDCl_3$),

δ 140.9, 136.1 (C-3 or C-5), 92.9 (C-4), [19.2 (CH_3), not observed (CH_2 - CH_2) (Et)]; ^{199}Hg NMR (δ) –895.3; IR: 3133w ν (C–H), 2461m ν (B–H), 1510m (ring breathing), 610s ν (Hg–C).

3.2.2.13. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]isopropylmercury

Compound 13, (TP^{4Br} -Hg-*i*-Pr). Yield: 547 mg (79%); m.p. 89–91°C. (Found: C, 21.04; H, 2.16; N, 11.81. Calcd. for $C_{12}H_{14}N_6BBr_3Hg$: C, 20.80; H, 2.04; N, 12.13). NMR: 1H ($CDCl_3$) δ 7.70, 7.49 (s, H-3 or H-5), [1.62, 2.57 *i*-Pr]; ^{13}C ($CDCl_3$) δ 141.0, 136.2 (C-3 or C-5), 93.4 (C-4), [25.8 (CH_3), not observed (CH), (*i*-Pr)]; ^{199}Hg NMR (δ) –1087.2; IR: 3135w ν (C–H), 2464w ν (B–H), 1512w (ring breathing), 610s ν (Hg–C).

3.2.2.14. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]phenylmercury

Compound 14, (TP^{4Br} -Hg-Ph). Yield: 406 mg (56%); m.p. 87–89°C. (Found: C, 24.20; H, 1.74; N, 10.98. Calcd. for $C_{15}H_{12}N_6BBr_3Hg$: C, 24.79; H, 1.66; N, 11.56). The compound is stable in the solid state only; it quickly decomposes in common organic solvents. IR: 3126w ν (C–H), 2467w ν (B–H), 1515w (ring breathing), 611s ν (Hg–C).

3.2.2.15. Hydridotris(4-bromo-1H-pyrazol-1-yl)borato]cyanomercury

Compound 15, (TP^{4Br} -Hg-CN). Yield: 574 mg (85%); char without melting; M.W. (Found/Calcd.) 686/675.7 (Found: C, 18.14; H, 1.13; N, 14.44. Calcd. for $C_{10}H_7N_7BBr_3Hg$: C, 17.78; H, 1.04; N, 14.51). NMR: 1H ($CDCl_3$) δ [7.75, 6.84 (s, H-3 or H-5), ($|^2J| = 4.9$ Hz, $|^3J| = 8.2$ Hz)]; ^{13}C ($CDCl_3$) δ 142.0, 136.8 (C-3 or C-5), 93.8 (C-4), 134.5 (CN); ^{199}Hg NMR (δ) –1101.0; IR: 3125w ν (C–H), 2482w ν (B–H), 1516w (ring breathing), 610s ν (Hg–C).

3.3. X-ray analysis of [hydridotris(3,5-diphenyl-1H-pyrazol-1-yl)borato]ethylmercury

Details of the structure analysis are listed in Table 2. The compound was recrystallised from dichloromethane/acetonitrile (1:2 v/v). X-ray data were collected from a colourless prismatic crystal at room temperature on an Enraf-Nonius CAD3-F automatic diffractometer using $Cu-K\alpha$ graphite-monochromated radiation operating in the ω/θ scan mode. The unit cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the θ range $26 \leq \theta \leq 28^\circ$. Three monitoring reflections, measured every 500, showed insignificant intensity fluctuations. The structure was solved by the heavy atom method. At the end of the isotropic refinement a correction for absorption effects was applied according to Walker and

Stuart [37], by using the computer program DIFABS (max and min values of the absorption correction were 1.62 and 0.45).

The full-matrix least-squares refinement minimised the quantity $\sum w (\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02 F_o)^2 + 1.0]$ where σ is derived from counting statistics. All other non-hydrogen atoms were refined anisotropically.

The H-atoms, placed in calculated positions, were assigned isotropic thermal parameters 1.2 times larger than those of the carrier atoms and included in the final refinement as riding atoms. The final Fourier difference map showed no peaks greater than $1.20 \text{ e } \text{Å}^{-3}$. The largest shift to the esd ratio in the final cycle was 0.03. Owing to the polarity of $P 2_1 2_1 2_1$ space group, the absolute configuration of the structure was determined.

Neutral atomic scattering factors were taken from literature [38]. All calculations, carried out on a Vax 750 at the 'Centro Interdipartimentale di Metodologie Chimico-fisiche' of the University of Naples, were performed by using the Enraf-Nonius (SDP) set of programs [39].

A full lists of fractional coordinates, bond distances and angles, hydrogen atom parameters and anisotropic thermal parameters of the non-hydrogen atoms has been deposited as supplementary material.

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