

# Novel scorpionate ligands devoid of C–H bonds: $Bp^{Br_3}$ and $Tp^{Br_3}$

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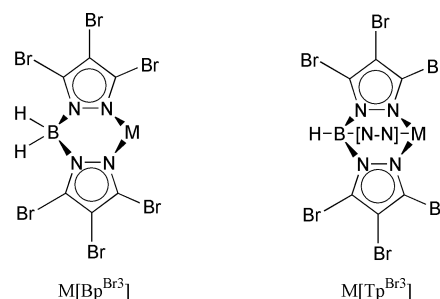
The novel ligands dihydrobis(3,4,5-tribromopyrazol-1-yl)borate,  $Bp^{Br_3}$ , and hydrotris(3,4,5-tribromopyrazol-1-yl)borate,  $Tp^{Br_3}$ , have been synthesized and structures of their complexes have been determined and compared with those of their almost isosteric  $Bp^*$  and  $Tp^*$  analogues. The structurally characterized complexes include  $Mo[Bp^{Br_3}](CO)_2(\eta^3\text{-methallyl})$ ,  $Mo[Bp^*](CO)_2(\eta^3\text{-methallyl})$ ,  $Mo[Tp^{Br_3}](CO)_2(\eta^3\text{-methallyl})$ ,  $Mo[Tp^*](CO)_2(\eta^3\text{-methallyl})$ ,  $Pd[Tp^{Br_3}](\eta^3\text{-methallyl})$ ,  $Pd[Tp^*](\eta^3\text{-methallyl})$ , and  $Rh[Tp^{Br_3}](CO)_2$ . The new ligands have the unique feature among scorpionates of containing no C–H bonds, thus making their organometallic derivatives more suitable for spectroscopic (IR, NMR) studies than those of other known  $Bp^x$  and  $Tp^x$  ligands.

## Introduction

Among the close to 180 scorpionate ligands known, the most frequently used has been, and still is,  $Tp^*$  ( $= [HB(3,5\text{-Me}_2\text{pz})_3]^-$ ) which, in terms of its steric effects, as expressed by its cone angle of  $239^\circ$ , fits about midway between the least hindered ligand, the parent  $Tp$  (cone angle  $183^\circ$ ) and the most hindered one,  $Tp^{Cy}$  (cone angle  $281^\circ$ ).<sup>1</sup> It is also very easy to synthesize from inexpensive starting materials. No wonder that it was the ligand of choice for a variety of studies. These included C–H bond activation catalysis by  $Rh[Tp^*](CO)_2$  and  $Rh[Tp^*](CO)(L)$  complexes, studied by Graham,<sup>2–5</sup> Lees,<sup>6–9</sup> and Bergman.<sup>10–12</sup> The use of  $Ir[Tp^*](CH_2=CH_2)_2$  in C–H bond activation by Carmona,<sup>13–18</sup> or of  $[Pt(Tp^*)Me_2]^-$  by Goldberg,<sup>19</sup> as well as McCleverty's studies on the construction of complicated polynuclear species with unusual non-linear optical properties based on the  $Tp^*Mo(NO)$  and  $Tp^*W(NO)$  cores,<sup>20</sup> and to a variety of other research areas such as, for instance, enzyme modeling. In other words, many researchers are quite familiar and comfortable with this ligand of intermediate steric hindrance which provides a relatively electron-enriched environment (as compared to the parent  $Tp$ ) to the coordinated metal, thanks to the inductive effect of the six methyl groups per  $Tp^*$ .

We wanted to introduce a new ligand, which would be sterically rather similar to  $Tp^*$ , and thus form structurally almost identical complexes, but would be electron-impoverished, as compared with the parent  $Tp$  or  $Tp^*$ . Moreover, we felt that it would be very useful to have a ligand devoid of C–H bonds, since this would permit spectroscopic studies (NMR, but especially IR) of organic residues bonded to the metal without the interfering C–H peaks due to the ligand. To this end the ligand hydrotris(3,4,5-tribromopyrazol-1-yl)borate,  $Tp^{Br_3}$ , the bromines of which are quite inert towards nucleophiles, was synthesized. It was also expected that the electron withdrawing effect of the nine bromines in the  $Tp^{Br_3}$  ligand would facilitate the detachment of one  $pz^{Br_3}$  arm, an established prerequisite in some C–H activation reactions by  $Tp^*Rh(CO)_2$ , and thus be useful in that area too. Researchers would then have a choice of sterically similar, but electronically quite different, homoscorpionate ligands at their disposal. A number of typical complexes based on  $Tp^{Br_3}$  were synthesized, structurally characterized, and compared to, and contrasted with, analogous complexes based on  $Tp^*$ .

We also synthesized the related heteroscorpionate ligand, dihydrobis(3,4,5-tribromopyrazol-1-yl)borate,  $Bp^{Br_3}$ , which is an analogue of  $Bp^*$ , and compared the two ligands within the structures of the complex pair  $Mo[Bp^{Br_3}](CO)_2(\eta^3\text{-methallyl})$ , **1**, and  $Mo[Bp^*](CO)_2(\eta^3\text{-methallyl})$ , **2**.



–[N–N]– is the third, hidden, 3,4,5-tribromopyrazolyl group

## Experimental

All chemicals were of the highest commercial reagent grade and were used as received. The compounds  $Mo(CO)_2(\eta^3\text{-methallyl})(Cl)(MeCN)_2$ ,<sup>21</sup>  $[PdCl(\eta^3\text{-methallyl})_2]$ ,<sup>22</sup>  $Mo[Bp^*](CO)_2(\eta^3\text{-methallyl})$  (**2**),<sup>23</sup> and  $Mo[Tp^*](CO)_2(\eta^3\text{-methallyl})$  (**4**),<sup>24</sup> were prepared by the literature procedures. Elemental analyses were done by Microanalysis, Inc., Wilmington, DE. Infrared spectra were obtained as Nujol mulls of KBr pellets with a Perkin-Elmer 1625 FTIR infrared spectrophotometer, using 16 scans. Proton NMR spectra were obtained in  $CDCl_3$  with a Nicolet NT360WB spectrometer. The compounds were studied with typical conditions of 16k data points, a sweep width of 3000–4000 Hz,  $90^\circ$  pulse angles, and a recycle time of 4–5 s.

## Syntheses

**3,4,5-Tribromopyrazole.** To a stirred solution of 35 g (0.5 mol) pyrazole and 80 g (2 mol) NaOH in 2 L water was added dropwise, over 1 h, 240 g (1.5 mol) bromine. The colorless solution containing a small amount of tan particles was filtered through Celite, and made strongly acid with concentrated HCl. This resulted in the precipitation of 3,4,5-tribromopyrazole, and the very thick slurry was stirred for a

further hour and then filtered. The solid was pressed down on the filter funnel, and washed with four 1 L portions of water. The still moist solid was stirred in 2 L chloroform, and the residual water separated out. The organic layer was passed through a bed of alumina, and distilling out the solvent produced 3,4,5-tribromopyrazole in 134 g (88%) yield. It was purified further by sublimation *in vacuo*. Its properties corresponded to literature values.<sup>25</sup>

**Na[Bp<sup>Br3</sup>]**. A mixture of 33.6 g (0.11 mol) 3,4,5-tribromopyrazole and 2.0 g (0.05 mol) NaBH<sub>4</sub> was stirred and refluxed in 300 mL DMF until the theoretical amount of hydrogen, as measured with a wet-test-meter, was evolved. The solvent was removed *in vacuo* and the crude product, obtained in 47 g (98%) yield, was recrystallized once from toluene, dried, and used for the preparation of derivatives without any additional purification.

**Na[Tp<sup>Br3</sup>]**. A mixture of 61 g (0.20 mol) tribromopyrazole and 2.0 g (0.05 mol) NaBH<sub>4</sub> was melted and heated in an oil bath up to 270 °C until cessation of hydrogen evolution. Excess tribromopyrazole was sublimed out *in vacuo*. The cooled crude product was removed mechanically, crushed, and more 3,4,5-tribromopyrazole was sublimed out until sublimation ceased. The crude Na[Tp<sup>Br3</sup>], obtained in 45.6 g (96%) yield, was used for derivative preparation without any additional purification.

**Tl[Tp<sup>Br3</sup>]**. A mixture of 9.5 g (10 mmol) Na[Tp<sup>Br3</sup>] and 2.66 g (10 mmol) TlNO<sub>3</sub> was stirred vigorously for 2 h in a mixture of 100 mL water and 100 mL chloroform. By that time the solid TlNO<sub>3</sub> had disappeared. The phases were separated, and evaporation of the chloroform layer produced Tl[Tp<sup>Br3</sup>] in 10.4 g (92%) yield. It was recrystallized from toluene. Mp 267–269 °C; IR: (BH) 2550 cm<sup>-1</sup>; <sup>13</sup>C NMR: 97.50 (C-4), 120.09 (C-5), 127.06 (C-3) ppm. The peak assignment was based on values calculated by the additive method.<sup>26</sup> Calc. for C<sub>9</sub>HBBBr<sub>9</sub>N<sub>6</sub>Tl: C 11.0, H 0.08, N 7.44. Found: C 11.3, H 0.29, N 7.23%.

**Mo[Bp<sup>Br3</sup>](CO)<sub>2</sub>(η<sup>3</sup>-methallyl), 1**. A mixture of 1.9 g (2 mmol) Na[Bp<sup>Br3</sup>] and 0.65 g (2 mmol) Mo(CO)<sub>2</sub>(η<sup>3</sup>-methallyl)Cl(MeCN)<sub>2</sub> was stirred for 1 h in 50 mL chloroform. 50 mL of water was then added, and the organic layer was chromatographed on alumina, collecting the red band. The product was obtained in 1.30 g (78%) yield, and was purified by recrystallization from toluene–heptane (1 : 1). Mp (dec.) 191–193 °C; IR: (BH) 2532, (CO) 1958, 1878 cm<sup>-1</sup>; <sup>1</sup>H NMR: broad peaks at 1.64 (2 H, *anti*) and 3.41 (2 H, *syn*), 1.81 (s, 3 H, Me) ppm. Calc. for C<sub>12</sub>H<sub>9</sub>BBBr<sub>6</sub>MoN<sub>4</sub>O<sub>2</sub>: C 17.4, H 1.10, N 6.76. Found: C 17.6, H 1.38, N 6.59%.

**Mo[Tp<sup>Br3</sup>](CO)<sub>2</sub>(η<sup>3</sup>-methallyl), 3**. A mixture of 2.26 g (1 mmol) Na[Tp<sup>Br3</sup>] and 0.65 g (2 mmol) Mo(CO)<sub>2</sub>(η<sup>3</sup>-methallyl)Cl(MeCN)<sub>2</sub> was stirred for 1 h in 50 mL chloroform. 50 mL of water was then added, and the organic layer was chromatographed on alumina, collecting the bright yellow band. The product was obtained in 1.61 g (72%) yield, and was purified by recrystallization from toluene. It melts gradually with decomposition from 220 °C; IR: (BH) 2590, (CO) 1958, 1870 cm<sup>-1</sup>; <sup>1</sup>H NMR: 3.91 (s, 2 H, *syn*), 1.73 (s, 2 H, *anti*), 1.37 (s, 3 H, Me) ppm; <sup>13</sup>C NMR: 19.83 (Me), 66.50 (CH<sub>2</sub>), 102.1 (C-4'), 104.38 (C-4), 124.7 (C-5'), 126.90 (C-5), 136.11 (C-3), 138.3 (C-3'), 201.00 (CO) ppm. The primed peaks belong to the unique pyrazolyl arm. Calc. for C<sub>15</sub>H<sub>8</sub>BBBr<sub>9</sub>N<sub>6</sub>MoO<sub>2</sub>: C 15.9, H 0.07, N 7.43. Found: C 16.2, H 0.26, N 7.15%.

**Pd[Tp<sup>Br3</sup>](η<sup>3</sup>-methallyl), 5**. A mixture of 2.26 g (2 mmol) Tl[Tp<sup>Br3</sup>] and 0.40 g (2 mmol) PdCl(η<sup>3</sup>-methallyl) was stirred in 50 mL chloroform for 1 h. The finely divided TlCl precipitate was removed from the slurry by passing through a layer of Celite, and evaporation of the filtrate gave Pd[Tp<sup>Br3</sup>](η<sup>3</sup>-

methallyl) in 1.83 g (84%) yield. It was recrystallized from toluene–heptane (1 : 1). Mp dec. from 184 °C; IR: (BH) 2538 cm<sup>-1</sup>; <sup>1</sup>H NMR: 2.21 (s, 3 H, Me), 3.09 (s, 2 H, *anti*), 4.33 (s, 2 H, *syn*) ppm; <sup>13</sup>C NMR: 22.5 (Me), 60.8 (CH<sub>2</sub>), 101.1 (C-4), 123.7 (C-5), 131.7 (C-3) ppm. Calc. for C<sub>13</sub>H<sub>8</sub>BBBr<sub>9</sub>N<sub>6</sub>Pd: C 14.4, H 0.007, N 7.74. Found: C 14.5, H 0.19, N 7.61%.

**Pd[Tp\*](η<sup>3</sup>-methallyl), 6**. The above procedure was repeated, but using TlTp\* instead of Tl[Tp<sup>Br3</sup>]. The product was obtained in 85% yield and was recrystallized from toluene. Mp dec. from 162 °C; IR: (BH) 2447 cm<sup>-1</sup>; <sup>1</sup>H NMR: 5.81 (s, 3 H, H-4), 3.78 (s, 2 H, *syn*), 2.63 (s, 2 H, *anti*), 2.28 (s, 9 H, Me), 2.20 (s, 9 H, Me), 2.09 (s, 3 H, η<sup>3</sup>-methallyl Me) ppm; <sup>13</sup>C NMR: 12.8 (pz-Me), 14.9 (pz-Me), 22.9 (η<sup>3</sup>-methallyl Me), 55.6 (CH<sub>2</sub>), 105.3 (C-4), 144.7 (C-5), 148.2 (C-3) ppm. Calc. for C<sub>19</sub>H<sub>29</sub>BN<sub>6</sub>Pd: C 36.6, H 7.76, N 23.3. Found: C 36.8, H 7.90, N 23.1%.

**Rh[Tp<sup>Br3</sup>](CO)<sub>2</sub>, 7**. A mixture of 1.13 g (1 mmol) Tl[Tp<sup>Br3</sup>] and 0.2 g (1 mmol) RhCl(CO)<sub>2</sub> was stirred in 50 mL chloroform for 1 h. The precipitated TlCl was removed by filtering the slurry through a layer of Celite, and evaporation of the filtrate gave Rh[Tp<sup>Br3</sup>](CO)<sub>2</sub> in 0.81 g (77%) yield. It was recrystallized from toluene. Mp 230–232 °C. IR: (BH) 2585, (CO) 2080, 2012 cm<sup>-1</sup>; <sup>13</sup>C NMR: 102.2 (C-4), 124.5 (C-5), 133.3 (C-3), 183.9 (*J* <sup>13</sup>C–<sup>103</sup>Rh = 72 Hz) (CO) ppm. Calc. for C<sub>11</sub>HBBBr<sub>9</sub>N<sub>6</sub>O<sub>2</sub>Rh: C 12.6, H 0.001, N 7.99. Found: C 12.8, H 0.23, N 7.73%.

**Co[Tp<sup>Br3</sup>]**. To a solution of 22 mmol crude Na{Tp<sup>Br3</sup>} in 50 mL DMF was added a concentrated aqueous solution of 10 mmol Co(ClO<sub>4</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>6</sub>. After stirring for 2 h, 300 mL water was added, and the yellow precipitate was filtered. The product was washed thoroughly with water and with methanol, and was obtained, in 86% yield after drying. It was recrystallized from xylene; mp none up to 308 °C; IR: (BH) 2588 cm<sup>-1</sup>. Calc. for C<sub>18</sub>H<sub>2</sub>B<sub>2</sub>Br<sub>18</sub>CoN<sub>12</sub>: C 11.3, H 0.00, N 8.81. Found: C 11.5, H 0.19, N 8.57%.

**Mo[Tp<sup>Br3</sup>](CO)<sub>2</sub>NO**. This compound was prepared by the method used for synthesizing Mo[Tp\*](CO)<sub>2</sub>NO,<sup>35</sup> and was obtained, after purification by chromatography on alumina, as a bright orange solid, mp: gradually darkens and dec. from about 290 °C; IR: (BH) 2597, (CO) 2025, 1936, (NO) 1688 cm<sup>-1</sup>. Calc. for C<sub>11</sub>HBBBr<sub>9</sub>MoN<sub>7</sub>O<sub>3</sub>: C 12.0, H 0.00, N 8.91. Found: C 12.3, H, 0.24, N 8.87%.

**W[Tp<sup>Br3</sup>](CO)<sub>2</sub>NO**. This compound was prepared by the method used for synthesizing W[Tp\*](CO)<sub>2</sub>NO,<sup>35</sup> and it was obtained, after purification by chromatography on alumina, as a bright orange solid, mp: none up to 308 °C; IR: (BH) 2600, (CO) 2013, 1923, (NO) 1677 cm<sup>-1</sup>. Calc. for C<sub>11</sub>HBBBr<sub>9</sub>N<sub>7</sub>O<sub>3</sub>W: C 11.1, H 0.00, N 8.25. Found: C 11.2, H 0.27, N 8.21%.

#### Crystallographic structural determination

Crystal data collection and refinement parameters are given in Table 1. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of a fine glass. Data were collected with a Siemens P4 diffractometer equipped with a Siemens P4/CCD diffractometer using graphite-monochromated Mo-Kα X-radiation (λ = 0.7173 Å).

The diffraction data of **2**, **3**, **4**, **6** and **7** are uniquely consistent with the reported space groups and yielded chemically reasonable and computationally stable results of refinement. No symmetry higher than triclinic was observed in the diffraction data of **1**, and **5**. In both cases the *E*-statistics suggested the centro-symmetric space group option, *P* $\bar{1}$ . Structure **6** was solved using the Patterson function and all other structures were solved by direct methods. All structures were completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. An empirical absorption correction was applied to the data of **1** and **5**, based on a Fourier

**Table 1** Crystal data collection and refinement details

Compound	1	2	3·CH <sub>2</sub> Cl <sub>2</sub>	4	5	6	7
Formula	C <sub>12</sub> H <sub>9</sub> BBr <sub>6</sub> - MoN <sub>4</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>23</sub> - BMoN <sub>4</sub> O <sub>2</sub>	C <sub>16</sub> H <sub>10</sub> BBr <sub>3</sub> Cl <sub>2</sub> - MoN <sub>6</sub> O <sub>2</sub>	C <sub>21</sub> H <sub>29</sub> BMoN <sub>6</sub> O <sub>2</sub>	C <sub>13</sub> H <sub>8</sub> BBr <sub>9</sub> N <sub>6</sub> Pd	C <sub>19</sub> H <sub>29</sub> BN <sub>6</sub> Pd	C <sub>11</sub> HBBr <sub>9</sub> - N <sub>6</sub> O <sub>2</sub> Rh
Formula weight	827.44	410.13	1215.14	504.24	1084.65	458.69	1082.09
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pbcn</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>I</i> 2/ <i>a</i>
<i>a</i> /Å	8.5258(2)	9.9584(5)	19.3440(11)	10.2604(6)	10.1589(3)	16.0102(8)	16.7656(16)
<i>b</i> /Å	10.3977(2)	14.4109(8)	20.8714(12)	27.6907(16)	10.4504(3)	8.4061(4)	14.2673(13)
<i>c</i> /Å	13.2707(3)	12.9238(7)	16.7739(9)	8.7327(5)	12.6714(3)	17.2544(9)	20.937(2)
$\alpha$ /°	87.2664(11)	—	—	—	101.967(2)	—	—
$\beta$ /°	86.3381(8)	103.5410(10)	—	114.8130(10)	92.483(2)	114.7850(10)	112.287(2)
$\gamma$ /°	69.5095(7)	—	—	—	104.979(2)	—	—
<i>V</i> /Å <sup>3</sup>	1099.35(6)	1803.13(17)	6772.2(7)	2252.1(2)	1264.60(6)	2108.25(18)	4634.0(8)
<i>Z</i> , <i>Z'</i>	2, 1	4, 1	8, 1	4, 1	2, 1	4, 1	8, 1
Crystal color, habit	Orange, block	Red, block	Yellow, block	Yellow, block	Pale yellow, plate	Colorless, block	Yellow, block
<i>D</i> <sub>s</sub> /g cm <sup>-3</sup>	2.500	1.511	2.384	1.487	2.849	1.445	3.102
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	115.15	7.43	111.91	6.13	149.67	8.96	162.81
<i>T</i> /K	223(2)	173(2)	293(2)	173(2)	173(2)	173(2)	173(2)
<i>R</i> ( <i>F</i> ), % <sup>a</sup>	6.71	2.98	5.09	4.80	3.77	3.12	3.09
<i>R</i> ( <i>W</i> <i>F</i> <sup>2</sup> ), % <sup>a</sup>	16.77	8.36	13.20	14.50	8.75	6.90	7.09

<sup>a</sup> Quantity minimized =  $R(WF^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ ;  $R = \sum \Delta I / \sum (F_o)$ ,  $\Delta = |F_o - F_c|$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$ .

series in the polar angles of the incident and diffracted beam paths and was used to model an absorption surface for the difference between the observed and calculated structure factors.<sup>36</sup> The positions of all borato protons, except those in **1**, were determined from the electron difference map, and the isotropic displacement coefficients were allowed to refine freely. All non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms, with the exceptions noted, were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL program libraries (G. M. Sheldrick, Siemens XRD, Madison, WI).

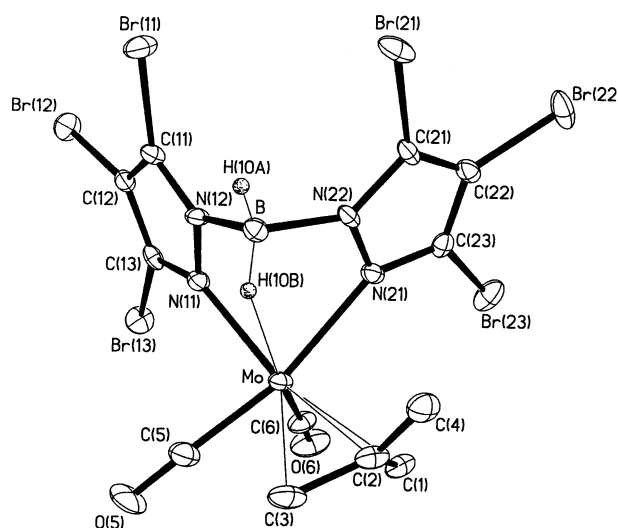
CCDC reference numbers 172549–172555.

See <http://www.rsc.org/suppdata/dt/b1/b111568p/> for crystallographic data in CIF or other electronic format.

## Results and discussion

The Bp<sup>Br3</sup> and Tp<sup>Br3</sup> ligands were synthesized in the conventional manner,<sup>1</sup> by the reaction of NaBH<sub>4</sub> with excess tribromopyrazole in DMF (for Bp<sup>Br3</sup>) or neat (for Tp<sup>Br3</sup>). The latter was characterized as Tl[Tp<sup>Br3</sup>]. The bromine atoms in 3,4,5-tribromopyrazole are remarkably inert towards nucleophiles, and this augured well for the stability in this particular respect of the ligands Bp<sup>Br3</sup> and Tp<sup>Br3</sup>. The structures of TlTp\* and Tl[Tp<sup>Br3</sup>] had been determined earlier,<sup>27</sup> and the cone angles based thereon were found to be 239° and 234°, respectively, and thus fairly similar, especially when compared to those of TlTp (183°) or Tl[Tp<sup>IBu</sup>] (253°). We proceeded to prepare a variety of pairs of representative complexes which were structurally characterized, and then compared them with their known counterparts based on Bp\* or Tp\*.

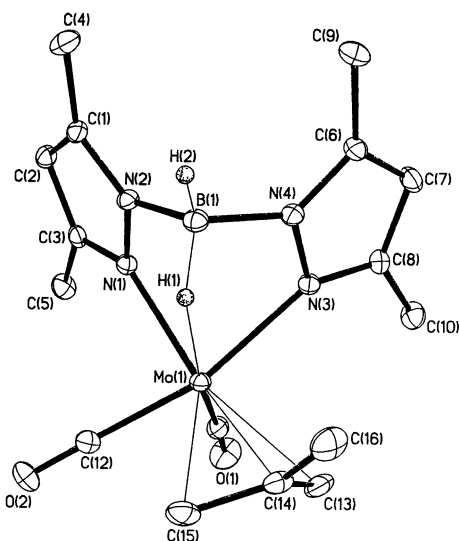
Only one complex pair was synthesized for the comparison of Bp<sup>Br3</sup> and Bp\*, namely Mo[Bp<sup>Br3</sup>](CO)<sub>2</sub>( $\eta^3$ -methallyl), **1**, and Mo[Bp\*](CO)<sub>2</sub>( $\eta^3$ -methallyl), **2**. Complexes **1** and **2** were isostructural. They both contained an agostic B–H–Mo bond, and were devoid of symmetry in the crystal, as in both compounds the methallyl group was asymmetrically disposed with respect to the boron–molybdenum axis (Figs. 1 and 2). However, in solution both structures were stereochemically non-rigid with temperature-dependent NMR spectra indicating **1** to have a somewhat lower rotational energy barrier than **2**. The N–Mo distances for **1** were 2.300 and 2.211 Å, with the shorter bond being *trans* to the  $\eta^3$ -methallyl group, and in **2** they were 2.209 and 2.181 Å, again, the shorter bond being *trans* to the  $\eta^3$ -methallyl group. The respective agostic B–H–Mo bond lengths



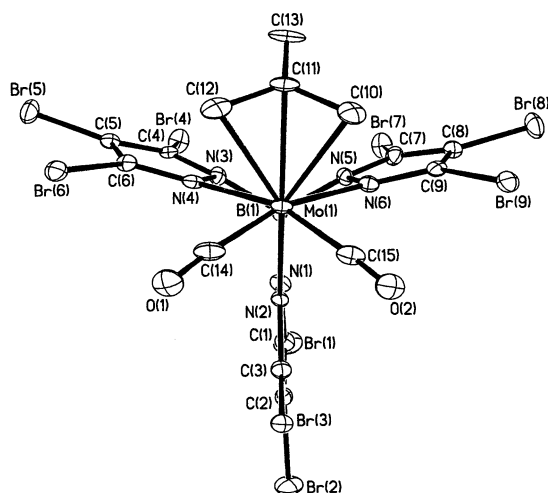
**Fig. 1** ORTEP<sup>37</sup> drawing of the structure of **1**. Selected bond distances (Å) and angles (°): Mo–N(11) 2.211(7), Mo–N(21) 2.300(7), Mo–C(1) 2.372(9), Mo–C(2) 2.779(9), Mo–C(3) 2.333(9); N(11)–Mo–N(21) 81.3(2), C(5)–Mo–C(6) 80.6(4), C(5)–Mo–N(11) 86.4(3), C(6)–Mo–N(11) 99.6(3), C(5)–Mo–C(2) 104.6(4).

for **1** and **2** were 2.415 and 2.147 Å. This led to non-bonded B–Mo distances of 2.858 for **1** and 2.818 Å for **2**, implying a looser structure in the case of the Bp<sup>Br3</sup> complex.

Since Tp\* was employed far more often than Bp\*, we synthesized several pairs of related Tp<sup>Br3</sup> and Tp\* compounds. One pair consisted of the molybdenum carbonyl complexes Mo[Tp<sup>Br3</sup>](CO)<sub>2</sub>( $\eta^3$ -methallyl), **3**, and Mo[Tp\*](CO)<sub>2</sub>( $\eta^3$ -methallyl), **4**. In both of them the ligands exhibited  $\kappa^3$  coordination. Both complexes were stereochemically rigid at room temperature, as indicated by their NMR spectra (<sup>1</sup>H and <sup>13</sup>C), which showed the presence of two identical and one different pyrazolyl arms. Their structures were very similar (Figs. 3 and 4). Each compound had a plane of symmetry, with the  $\eta^3$ -methallyl group symmetrically located between two pyrazolyl planes, straddling a C<sub>3</sub> plane. The Mo–N distances were 2.24, 2.33 and 2.33 Å in **3**, and 2.22, 2.31 and 2.30 Å in **4**. In each case, the short distance was that of the Mo–N bond *trans* to the  $\eta^3$ -methallyl group. The respective non-bonding Mo–B distances were 3.36 and 3.31 Å, again implying a looser structure for **3**. This was also demonstrated by the NMR spectra, where the  $\eta^3$ -methallyl peaks were moderately broadened for the Tp<sup>Br3</sup> complex, but very sharp for the Tp\* analogue.<sup>24</sup>



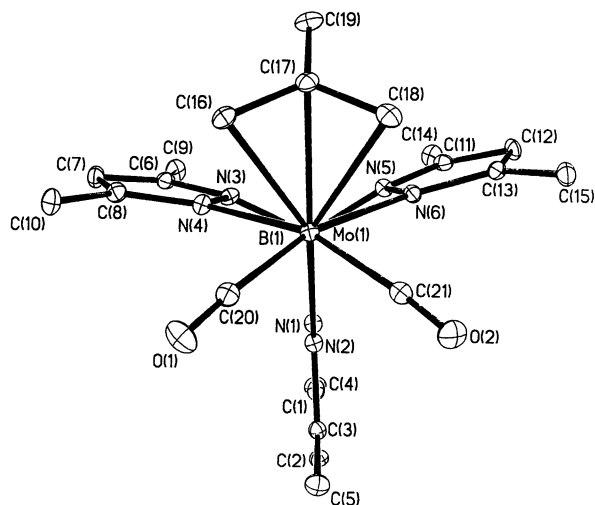
**Fig. 2** ORTEP drawing of the structure of **2**. Selected bond distances (Å) and angles (°): Mo–N(1) 2.181(2), Mo–N(3) 2.209(2), Mo–C(13) 2.349(3), Mo–C(14) 2.255(3), Mo–C(15) 2.303(3), Mo–H(1) 2.147(1); N(1)–Mo–N(3) 81.3(1), N(1)–Mo–C(12) 83.6(1), N(1)–Mo–C(14) 154.6(11), N(1)–Mo–C(15) 137.2(1).



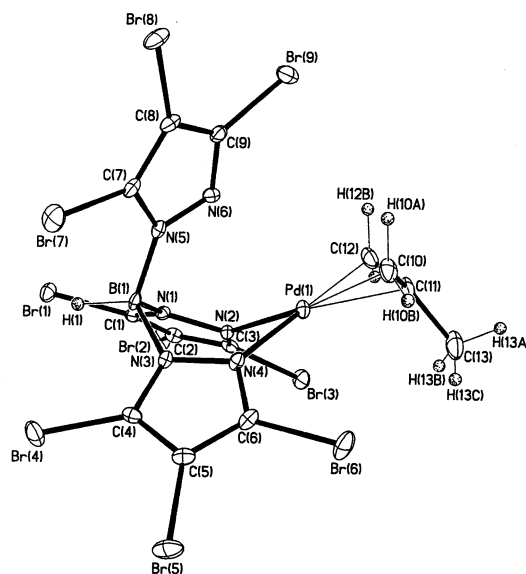
**Fig. 3** ORTEP drawing of the structure of **3**. Selected bond distances (Å) and angles (°): Mo–N(2) 2.236(6), Mo–N(4) 2.325(7), Mo–N(6) 2.334(7), Mo–C(10) 2.358(8), Mo–C(11) 2.244(8), Mo–C(12) 2.358(8); N(2)–Mo–N(4) 75.6(2), N(2)–Mo–N(6) 75.4(2), N(6)–Mo–N(4) 92.6(2).

Another pair of complexes compared, consisted of Pd[ $\text{Tp}^{\text{Br}_3}$ ]( $\eta^3$ -methallyl), **5**, and Pd[ $\text{Tp}^*$ ]( $\eta^3$ -methallyl), **6**, both of which were prepared by the method used to synthesize Pd[ $\text{Tp}$ ]( $\eta^3$ -allyl),<sup>28</sup> and each of them contained  $\kappa^2$  ligands with the third nitrogen uncoordinated (Figs. 5 and 6) in the solid state. Each ligand, however, underwent rapid exchange of the coordinated and uncoordinated pyrazolyl arms in solution, as demonstrated by their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which showed only one type of pyrazolyl group at room temperature. The Pd–N bonds in **5** were 2.12 and 2.13 Å, while in **6** both were 2.09 Å. A loosening of the structure in **5** was also indicated by the non-bonding B–Pd distance, which was 3.28 Å for **5** and 3.13 Å for **6**. The twist of the uncoordinated pyrazolyl group around the B–Pd axis was 49.4° for **5** and 74.9° for **6**, indicative of greater proximity of the potentially coordinating N to Pd in **5** (N–Pd distance 2.85 Å) than in **6** (N–Pd distance 3.34 Å).

We also prepared and structurally characterized the Rh(I) complex, Rh[ $\text{Tp}^{\text{Br}_3}$ ](CO)<sub>2</sub>, which contained five-coordinate rhodium, with two short (both 2.12 Å) and one long (2.52 Å) bonds (see Fig. 7). Although the complex Rh[ $\text{Tp}^*$ ](CO)<sub>2</sub> is well-known, and has often been used, it has never been structurally



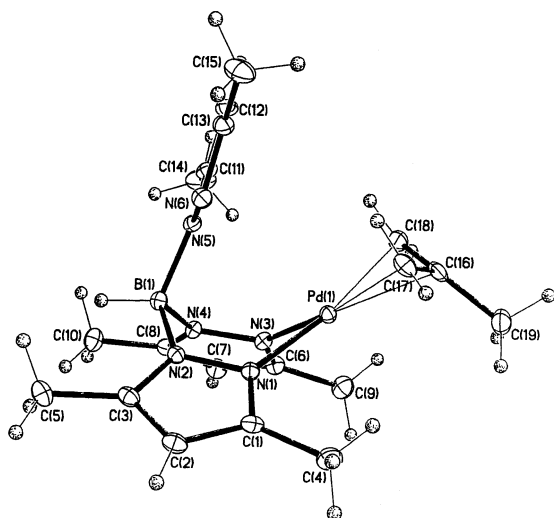
**Fig. 4** ORTEP drawing of the structure of **4**. Selected bond distances (Å) and angles (°): Mo–N(2) 2.218(4), Mo–N(4) 2.308(4), Mo–N(6) 2.301(4), Mo–C(16) 2.332(5), Mo–C(17) 2.249(5), Mo–C(18) 2.346(5); N(2)–Mo–N(4) 76.0(1), N(2)–Mo–N(6) 76.6(1), N(6)–Mo–N(4) 92.2(1).



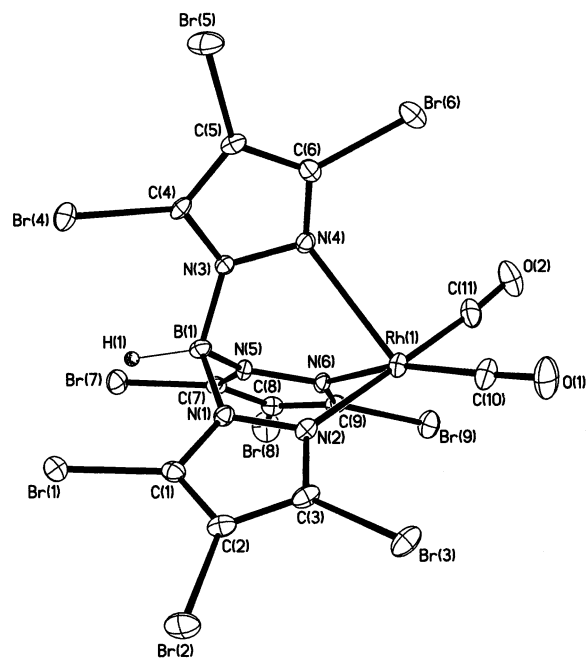
**Fig. 5** ORTEP drawing of the structure of **5**. Selected bond distances (Å) and angles (°): Pd–N(2) 2.127(4), Pd–N(4) 2.124(4), Pd–C(10) 2.103(6), Pd–C(11) 2.141(5), Pd–C(12) 2.107(6); N(2)–Pd–N(4) 85.0(2), N(2)–Pd–C(10) 169.2(2), N(2)–Pd–C(11) 133.9(2), N(2)–Pd–C(12) 101.7(2).

characterized. In the related complexes, the structures of which have been determined, and which contain a similar five-coordinate structure: Rh[ $\text{Tp}^{\text{CF}_3, \text{Me}^c}$ ](CO)<sub>2</sub>,<sup>29</sup> Rh[ $\text{Tp}^{\text{Ph}, \text{Me}^c}$ ](CO)<sub>2</sub>,<sup>30</sup> and Rh[HB(2*H*-benz(*g*)-4,5-dihydroindazol-2-yl)](CO)<sub>2</sub>,<sup>31</sup> the two short and one long Rh–N bonds were 2.10, 2.10, 2.62 Å; 2.09, 2.09, 2.78 Å, and 2.10, 2.10, 2.85 Å, respectively. The length disparity between the short and long Rh–N bonds was substantially larger in these complexes, than in Rh[ $\text{Tp}^{\text{Br}_3}$ ](CO)<sub>2</sub>. A comparison of the CO stretch of **7** (2080 and 2012 cm<sup>-1</sup>) with the  $\text{Tp}^*$  analogue (2054, 1981 cm<sup>-1</sup>),<sup>32</sup> showed a shift of about 30 cm<sup>-1</sup> towards higher frequency, while the  $^{13}\text{C}$ – $^{103}\text{Rh}$  coupling was 72 Hz, close to the value of 69 Hz found in Rh[ $\text{Tp}^*$ ](CO)<sub>2</sub>.<sup>33</sup>

In the compact octahedral complexes Co[ $\text{Tp}^{\text{Br}_3}$ ]<sub>2</sub>, and Co[ $\text{Tp}^*$ ]<sub>2</sub> the Co–N distances were all exactly 2.139 Å in the former complex, and ranged from 2.142 to 2.146 Å in the latter being, surprisingly, marginally shorter for Co[ $\text{Tp}^{\text{Br}_3}$ ]<sub>2</sub>. At the same time, this complex showed a slight departure from  $D_{3d}$  symmetry.<sup>34</sup> Other complexes, where  $\text{Tp}^{\text{Br}_3}$  and  $\text{Tp}^*$  ligands



**Fig. 6** ORTEP drawing of the structure of **6**. Selected bond distances (Å) and angles (°): Pd–N(1) 2.090(2), Pd–N(3) 2.086(2), Pd–C(16) 2.143(3), Pd–C(17) 2.114(3), Pd–C(18) 2.111(3); N(1)–Pd–N(3) 86.76(8), N(3)–Pd–C(16) 133.89(10), N(1)–Pd–C(16) 137.81(10).



**Fig. 7** ORTEP drawing of the structure of **7**. Selected bond distances (Å) and angles (°): Rh–N(2) 2.122(4), Rh–N(4) 2.523(4), Rh–N(6) 2.124(4), Rh–C(10) 1.847(5), Rh–C(11) 1.849(6); N(2)–Rh–N(4) 85.3(1), N(2)–Rh–N(6) 85.2(1), N(6)–Rh–N(4) 78.8(1).

were compared with reference to their CO and NO stretch frequencies, included the pairs Mo[ $\text{Tp}^{\text{Br}3}$ ](CO)<sub>2</sub>NO and Mo[ $\text{Tp}^*$ ](CO)<sub>2</sub>NO,<sup>35</sup> as well as W[ $\text{Tp}^{\text{Br}3}$ ](CO)<sub>2</sub>NO and W[ $\text{Tp}^*$ ](CO)<sub>2</sub>NO.<sup>35</sup> In each pair the CO and NO frequencies were always higher for the  $\text{Tp}^{\text{Br}3}$  complex. Specifically, for Mo[ $\text{Tp}^{\text{Br}3}$ ](CO)<sub>2</sub>NO, the values were 2025, 1936 and 1688 cm<sup>-1</sup>, while for Mo[ $\text{Tp}^*$ ](CO)<sub>2</sub>NO they were 2016, 1925 and 1673 cm<sup>-1</sup>, respectively. Similarly, in the case of the tungsten analogues, these values were 2013, 1923 and 1677 cm<sup>-1</sup> versus 2001, 1905 and 1662 cm<sup>-1</sup>.

## Conclusion

In summary, we have prepared novel and unique scorpionate ligands  $\text{Bp}^{\text{Br}3}$  and  $\text{Tp}^{\text{Br}3}$ , which contain no C–H bonds, and

which provide clear spectroscopic (IR and NMR) windows for the study of organometallic reactions in the C–H region. Moreover, these ligands are sterically similar to the long-favored  $\text{Bp}^*$  and  $\text{Tp}^*$  analogues, yet electronically different due to the presence of three bromines per pyrazolyl ring, which leads to a somewhat looser structure in their complexes. It might be of interest to compare the C–H bond activation ability of Rh[ $\text{Tp}^{\text{Br}3}$ ](CO)<sub>2</sub> with that of Rh[ $\text{Tp}^*$ ](CO)<sub>2</sub>.

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