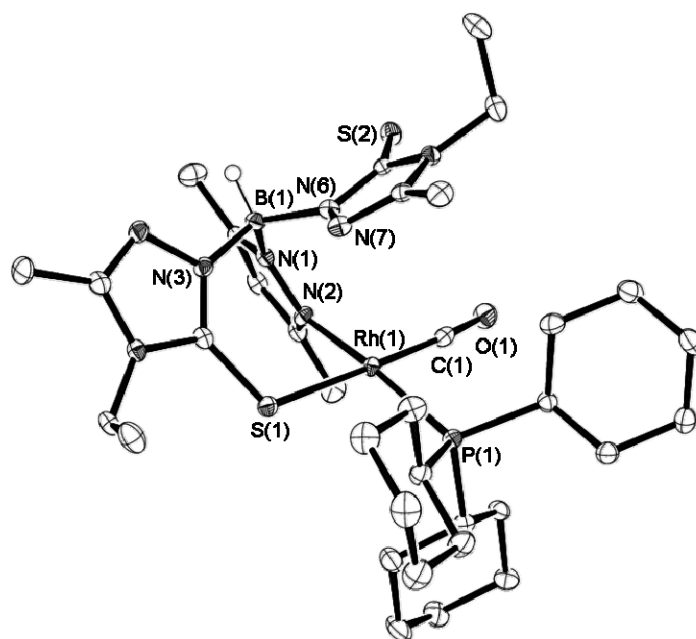
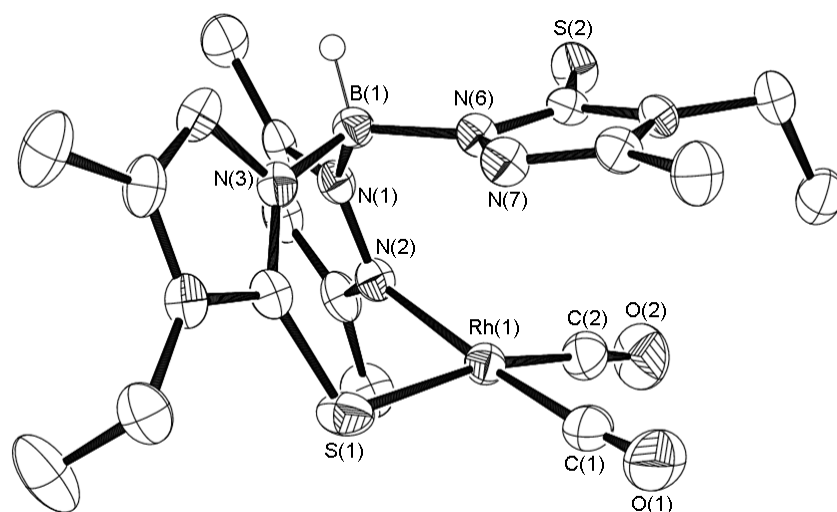


## Isomerism in rhodium(I) *N,S*-donor heteroscorpionates: ring substituent and ancillary ligand effects

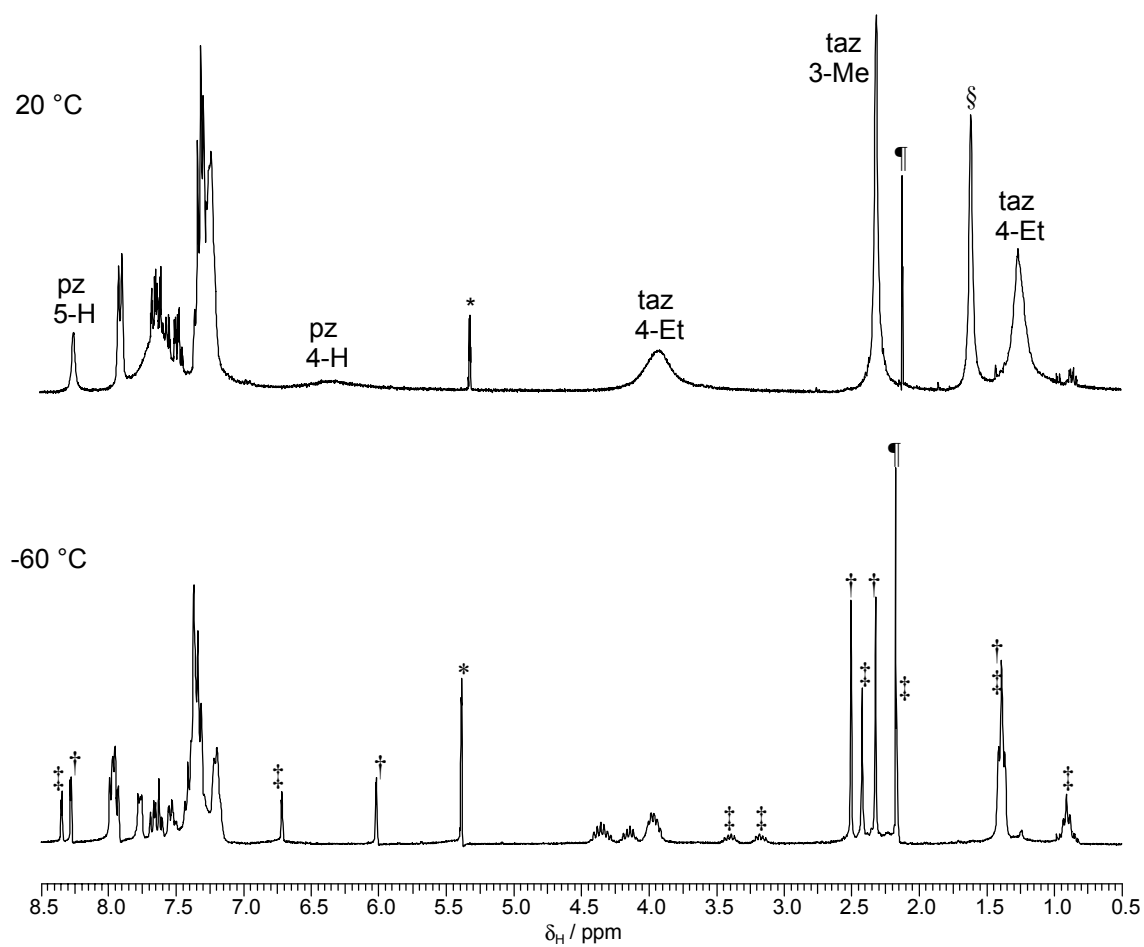
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**Figure S1** Molecular structure of  $[\text{Rh}(\text{CO})(\text{PCy}_3)\{\text{HB}(\text{taz})_2(\text{pz}^{\text{Me}_2})\}]$  **17**



**Figure S2** Molecular structure of  $[\text{Rh}(\text{CO})_2\{\text{HB}(\text{taz})_2(\text{pz}^{\text{Me}_2})\}]$  **10**



**Figure S3** Variable temperature <sup>1</sup>H NMR spectra of  $[\text{Rh}(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{taz})_2(\text{pz}^{\text{Ph}})\}]$  **21**, showing two isomers († and ‡), residual  $\text{CH}_2\text{Cl}_2/\text{CHDCl}_2$  (\*) and trace  $(\text{CH}_3)_2\text{CO}$  (¶)

**Table S1** Proton NMR spectroscopic data for **6**, **7** and **21** at low temperatures, showing multiple isomers († and ‡)<sup>a</sup>

Complex	
<b>6</b>	[Rh(cod){HB(taz) <sub>2</sub> (pz <sup>Me2</sup> )}]
	5.82 (s, 1H, pz 4- <i>H</i> ) <sup>†</sup> , 5.71 (s, 1H, pz 4- <i>H</i> ) <sup>‡</sup> , 4.95-3.93 (br m, 8H+8H, taz 4-CH <sub>2</sub> CH <sub>3</sub> & cod CH), 2.78-1.36 (br m, 8H+8H, cod CH <sub>2</sub> ), 2.47-2.25 (m, 12H+12H, pz 3/5-CH <sub>3</sub> & taz 3-CH <sub>3</sub> ), 1.24 (t, 3H, <sup>3</sup> J <sub>HH</sub> 7.0, taz 4-CH <sub>2</sub> CH <sub>3</sub> ), 1.15 (br t, 3H+6H, <sup>3</sup> J <sub>HH</sub> 7.0, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>b</sup>
<b>7</b>	[Rh(cod){HB(taz) <sub>2</sub> (pz <sup>Ph</sup> )}]
	8.73-7.88 (m, 5H+5H, pz 3- <i>Ph</i> ), 8.48 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.2, pz 5- <i>H</i> ) <sup>†</sup> , 8.36 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.4, pz 5- <i>H</i> ) <sup>‡</sup> , 6.73 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.2, pz 4- <i>H</i> ) <sup>†</sup> , 6.49 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.4, pz 4- <i>H</i> ) <sup>‡</sup> , 4.43-3.72 (br m, 8H+8H, taz 4-CH <sub>2</sub> CH <sub>3</sub> & cod CH), 3.58-1.42 (br m, 8H+8H, cod CH <sub>2</sub> ), 2.54 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>†</sup> , 2.37 (s, 6H, taz 3-CH <sub>3</sub> ) <sup>‡</sup> , 2.32 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>†</sup> , 1.37 (t, 3H, <sup>3</sup> J <sub>HH</sub> 7.0, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>†</sup> , 1.31 (t, 3H, <sup>3</sup> J <sub>HH</sub> 7.4, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>†</sup> , 1.24 (t, 6H, <sup>3</sup> J <sub>HH</sub> 6.9, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>‡b</sup>
<b>21</b>	[Rh(CO)(PPh <sub>3</sub> ){HB(taz) <sub>2</sub> (pz <sup>Ph</sup> )}]
	8.35 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.2 pz 5- <i>H</i> ) <sup>‡</sup> , 8.29 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.6 pz 5- <i>H</i> ) <sup>†</sup> , 8.03-7.12 (m, 20H+20H, PPh <sub>3</sub> & pz 3- <i>Ph</i> ), 6.72 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.2 pz 4- <i>H</i> ) <sup>‡</sup> , 6.02 (d, 1H, <sup>3</sup> J <sub>HH</sub> 2.6 pz 4- <i>H</i> ) <sup>†</sup> , 4.37 (q, 1H, <sup>3</sup> J <sub>HH</sub> 7.3, taz 4-CHHCH <sub>3</sub> ), 4.32 (q, 1H, <sup>3</sup> J <sub>HH</sub> 7.0, taz 4-CHHCH <sub>3</sub> ), 4.15 (q, 1H, <sup>3</sup> J <sub>HH</sub> 7.3, taz 4-CHHCH <sub>3</sub> ), 3.96 (m, 3H, taz 4-CHHCH <sub>3</sub> ), 3.40 (q, 1H, <sup>3</sup> J <sub>HH</sub> 6.9, taz 4-CHHCH <sub>3</sub> ) <sup>‡</sup> , 3.17 (q, 1H, <sup>3</sup> J <sub>HH</sub> 7.3, taz 4-CHHCH <sub>3</sub> ) <sup>‡</sup> , 2.50 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>†</sup> , 2.42 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>‡</sup> , 2.32 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>†</sup> , 2.16 (s, 3H, taz 3-CH <sub>3</sub> ) <sup>‡</sup> , 1.39 (t, 6H+3H, <sup>3</sup> J <sub>HH</sub> 7.0, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>†‡</sup> , 0.91 (t, 3H, <sup>3</sup> J <sub>HH</sub> 7.2, taz 4-CH <sub>2</sub> CH <sub>3</sub> ) <sup>‡c</sup>

<sup>a</sup> Chemical shift (δ) in ppm, *J* values in Hz, spectra in CD<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> At -80 °C. <sup>c</sup> At -60 °C.