A novel route to rhodaboratranes $[Rh(CO)(PR_3)\{B(taz)_3\}]^+$ *via* the redox activation of scorpionate complexes [RhLL'(Tt)]

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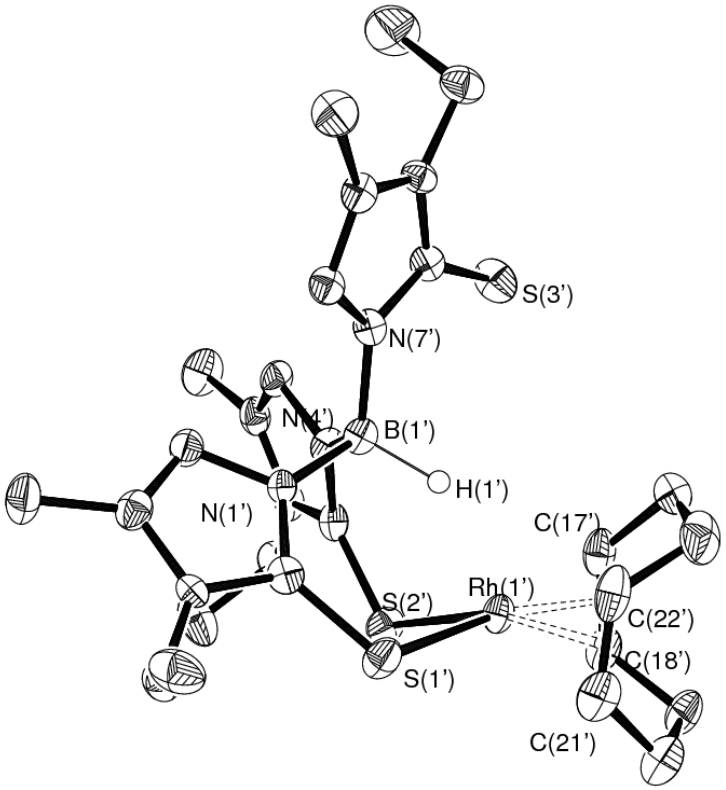

Figure S1 Molecular structure of [Rh(cod)Tt] **2**, second distinct structure in the unit cell. (Ellipsoids are shown at the 50% probability level; most hydrogen atoms are omitted for clarity).

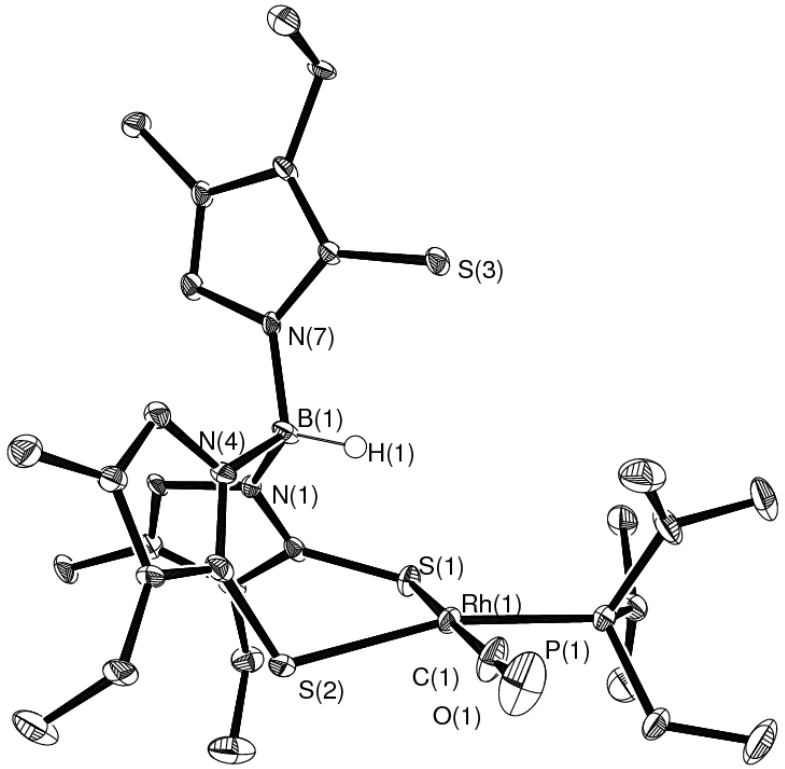

Figure S2 Molecular structure of [Rh(CO){P(NMe$_2$)$_3$}Tt] **7**. (Ellipsoids are shown at the 50% probability level; most hydrogen atoms are omitted for clarity).

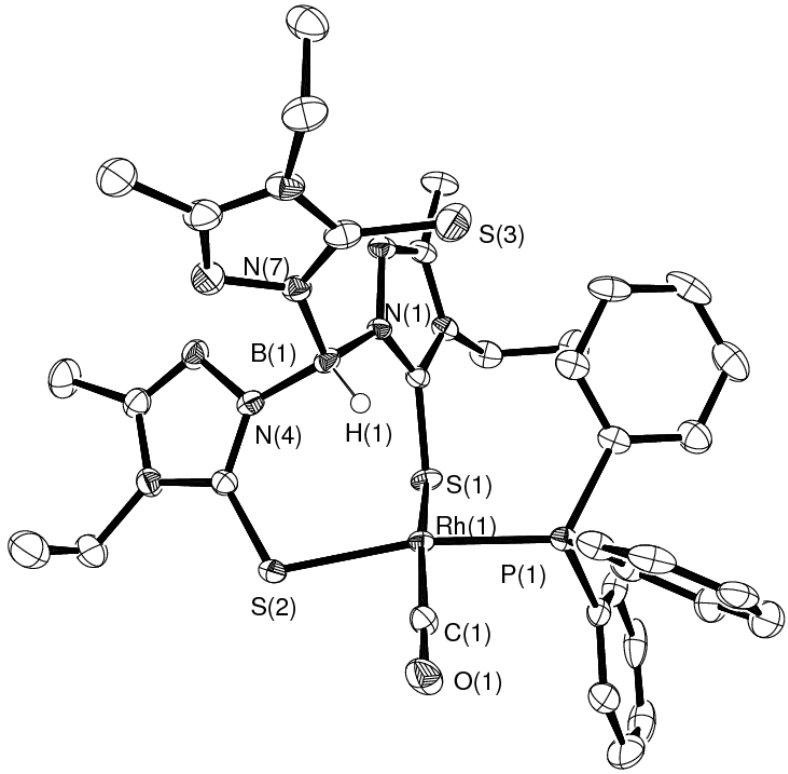

Figure S3 Molecular structure of [Rh(CO)(PPh$_3$)Tt] **8**. (Ellipsoids are shown at the 50% probability level; most hydrogen atoms are omitted for clarity).

Table S1 Proton NMR spectroscopic data for [Rh(cod)Tt] **2** and [Rh(CO)(PPh_3)Tt] **8** at –80 °C.[a]

Complex	
[Rh(cod)Tt] **2**	4.27 (br s, 4H, cod C*H*), 4.12 (q, 2H, $^3J_{HH}$ 7.0, Tt 4-CH_2CH$_3$), 4.05 (dq, 2H, $^2J_{HH}$ 14.2, $^3J_{HH}$ 7.0, Tt 4-C*H*HCH$_2$), 3.89 (dq, 2H, $^2J_{HH}$ 14.2, $^3J_{HH}$ 7.0, Tt 4-C*H*HCH$_2$), 2.84-2.64 (br m, 2H, cod CHH^{exo}), 2.43-2.33 (br m, 2H, cod CHH^{exo}), 2.42 (s, 3H, Tt 3-CH_3), 2.36 (s, 6H, Tt 3-CH_3), 1.88 (q, 2H, J_{HH} 8.0, cod CHH^{endo}), 1.78 (q, 2H, J_{HH} 7.7, cod CHH^{endo}), 1.33 (t, 3H, $^3J_{HH}$ 7.0, Tt 4-CH$_2$CH_3), 1.25 (t, 6H, $^3J_{HH}$ 7.0, Tt 4-CH$_2$CH_3)
[Rh(CO)(PPh_3)Tt] **8**	.84-7.31 (m, 15H, P*Ph*$_3$), 4.33 (dq, 1H, $^2J_{HH}$ 14.1, $^3J_{HH}$ 6.9, Tt 4-C*H*HCH$_3$), 4.23 (dq, 1H, $^2J_{HH}$ 13.7, $^3J_{HH}$ 6.6, Tt 4-C*H*HCH$_3$), 4.05 (dq, 1H, $^2J_{HH}$ 14.1, $^3J_{HH}$ 6.9, Tt 4-C*H*HCH$_3$), 3.97 (dq, 1H, $^2J_{HH}$ 13.7, $^3J_{HH}$ 6.6, Tt 4-C*H*HCH$_3$), 3.29 (dq, 1H, $^2J_{HH}$ 14.3, $^3J_{HH}$ 6.9, Tt 4-C*H*HCH$_3$), 3.11 (dq, 1H, $^2J_{HH}$ 14.3, $^3J_{HH}$ 6.9, Tt 4-C*H*HCH$_3$), 2.41 (s, 3H, Tt 3-CH_3), 2.39 (s, 3H, Tt 3-CH_3), 2.21 (s, 3H, Tt 3-CH_3), 1.37 (t, 3H, $^3J_{HH}$ 6.6, Tt 4-CH$_2$CH_3), 1.32 (t, 3H, $^3J_{HH}$ 6.9, Tt 4-CH$_2$CH_3), 0.86 (t, 3H, $^3J_{HH}$ 6.9, Tt 4-CH$_2$CH_3)

[a] Chemical shift (δ) in ppm, *J* values in Hz, spectra in CD_2Cl_2.

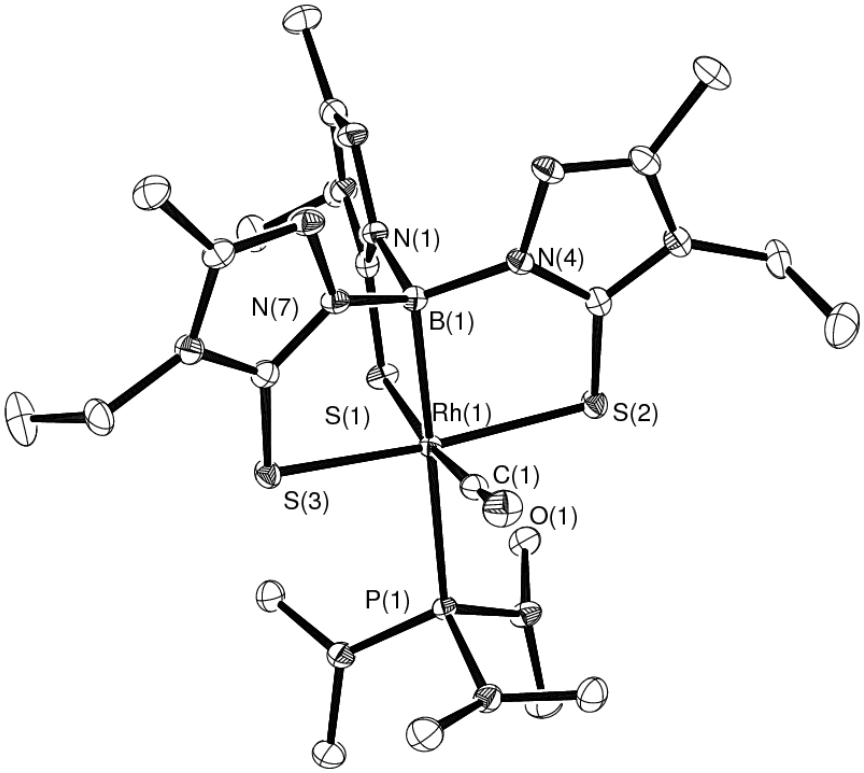

Figure S4 Structure of the cation $[Rh(CO)\{P(NMe_2)_3\}\{B(taz)_3\}]^+$ **12**$^+$. (Ellipsoids are shown at the 50% probability level; all hydrogen atoms are omitted for clarity).

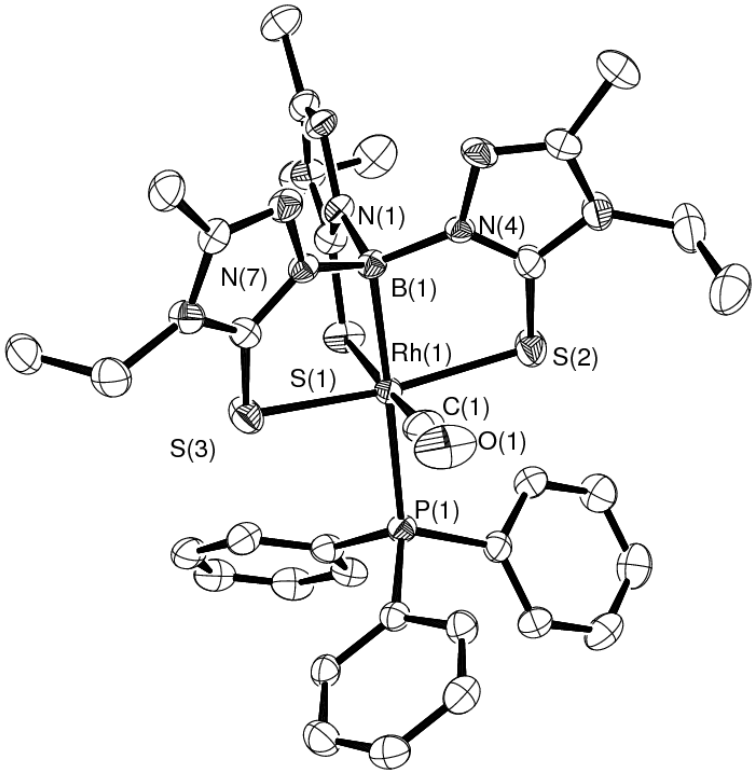

Figure S5 Structure of the cation $[Rh(CO)(PPh_3)\{B(taz)_3\}]^+$ **13**$^+$. (Ellipsoids are shown at the 50% probability level; all hydrogen atoms are omitted for clarity).