Unprecedented flexibility of the 1,1′-bis(*o*-carborane) ligand: catalytically-active species stabilised by B-agostic B–H→Ru interactions

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Electronic Supporting Information

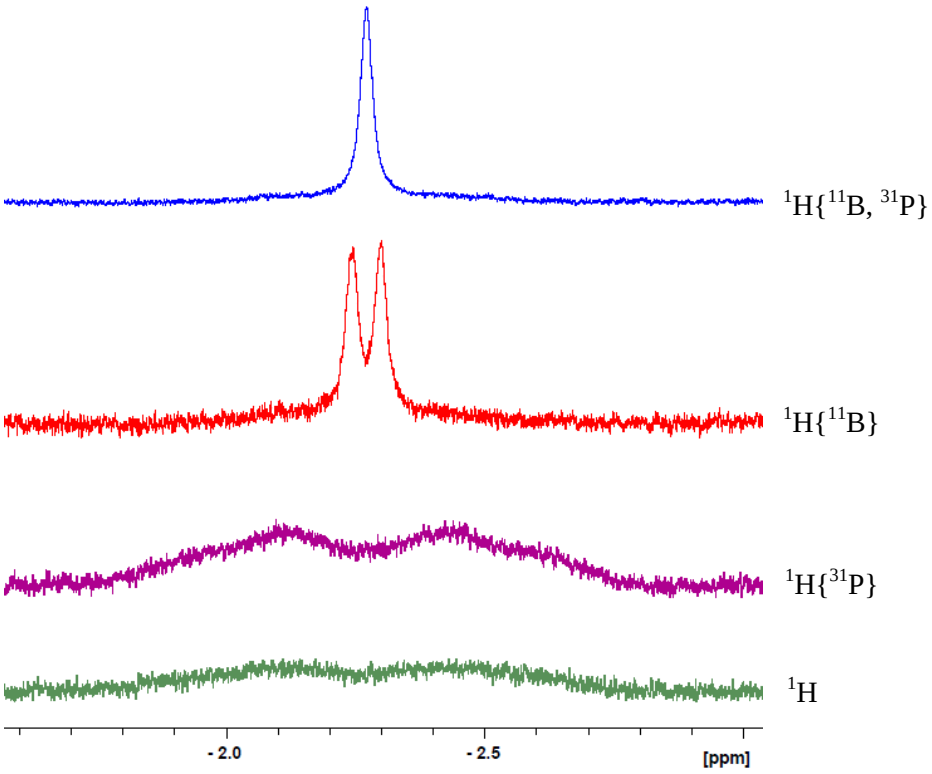
S1. NMR study of compound 4

Compounds **3** and **4** are fully analogous and have very similar NMR spectra. The signal for the agostic B*H* appears as two peaks in the $^{1}H\{^{11}B\}$ NMR spectrum, and this could be interpreted in two different ways: a doublet arising from coupling to one P atom or two singlets arising from two isomers of these compounds, one with C2' on the opposite side of the molecule from the agostic BH and the other with C2' on the same side.

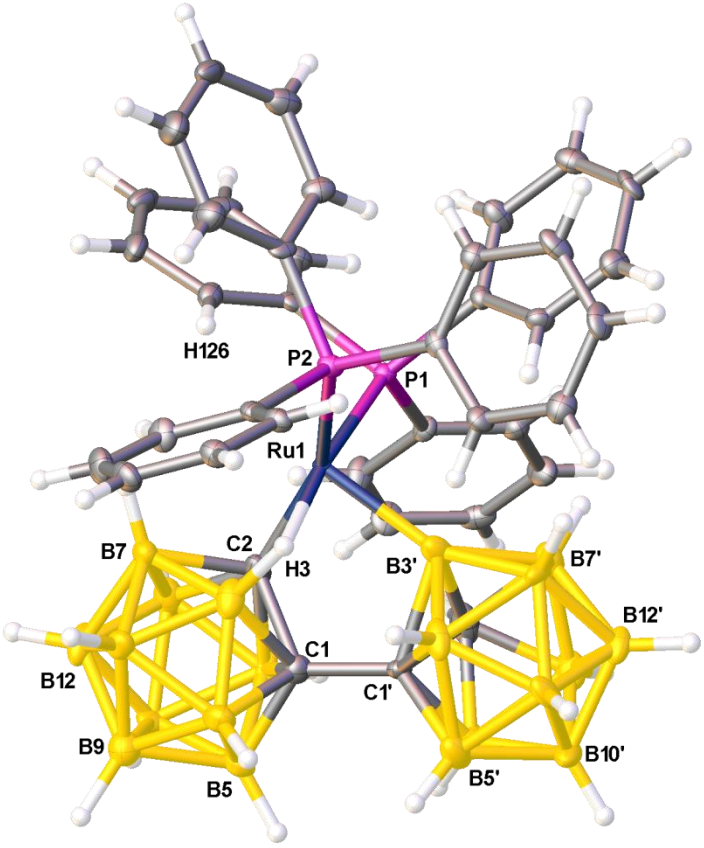
We initially believed that the second interpretation was correct, since;

- The ^{31}P NMR spectrum of **4** was effectively identical to the $^{31}P\{^{1}H\}$ spectrum.
- Both $^{1}H/^{31}P\{^{1}H\}$ HMBC and HMQC spectra of **4** revealed no evidence of coupling between the agostic B*H* and either P atom.

However, conclusive evidence that the first interpretation (the agostic B*H* resonance is a doublet arising from ^{31}P coupling) is correct was provided by $^{1}H\{^{11}B, ^{31}P\}$ NMR spectroscopy on compound **4**:

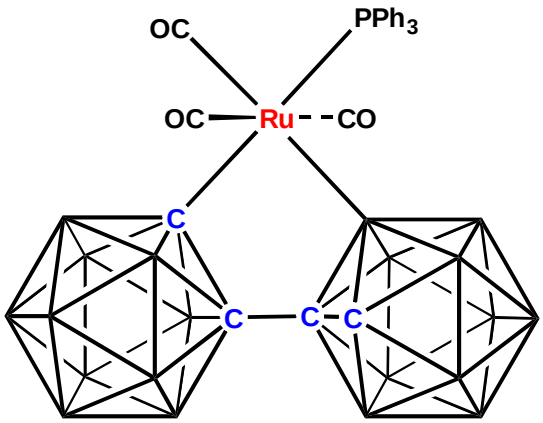


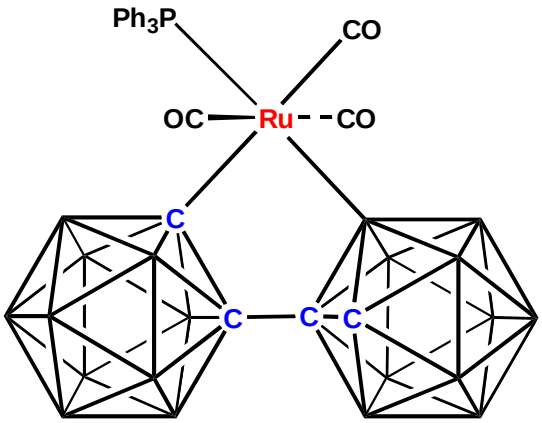
S2.



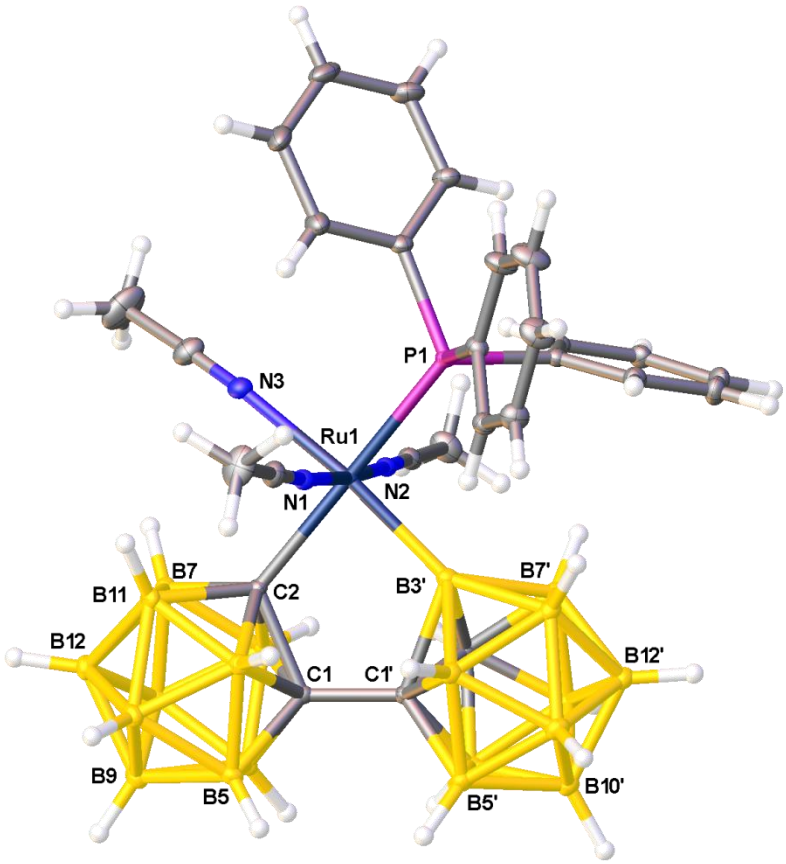
Perspective view of compound **3** and part of the atom numbering scheme. Only the major component of the partial disorder is shown. Selected interatomic distances (Å): Ru1–C2 2.131(6), Ru1–B3′ 2.108(7), Ru1–H3 1.79(6), Ru1–B3 2.422(7), B3–H3 1.14(6), Ru1–P1 2.2901(13), Ru1–P2 2.4480(13), C1–C1′ 1.526(7).

S3. The two isomers of compound 5



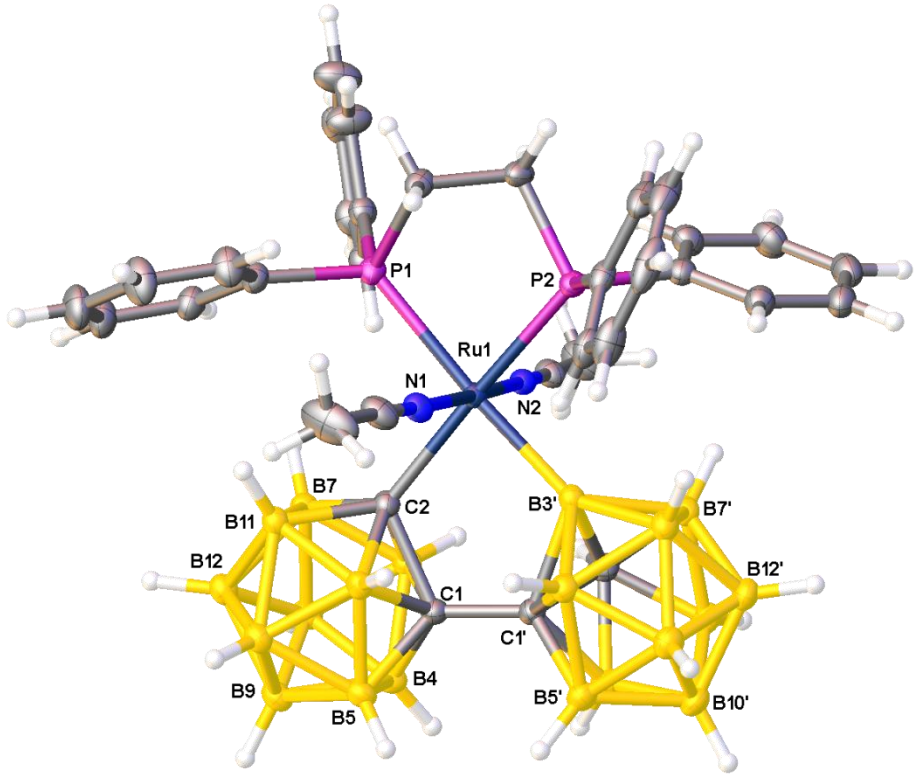


S4.



Perspective view of compound **6** and part of the atom numbering scheme. Selected interatomic distances (Å) and angles (°): Ru1–C2 2.1645(13), Ru1–B3′ 2.1019(16), Ru1–P1 2.3769(5), Ru1–N1 2.0191(13), Ru1–N2 2.0211(13), Ru1–N3 2.1769(13), C1–C1′ 1.5351(19), Ru1–N1–C11 174.25(12), Ru1–N2–C21 177.43(11), Ru1–N3–C31 160.66(13).

S5.



Perspective view of compound **8** and part of the atom numbering scheme. Selected interatomic distances (Å) and angles (°): Ru1–C2 2.1716(18), Ru1–B3′ 2.143(2), Ru1–P1 2.4256(5), Ru1–P2 2.3473(5), Ru1–N1 2.0188(17), Ru1–N2 1.9943(17), C1–C1′ 1.524(3), Ru1–N1–C11 174.30(18), Ru1–N2–C21 179.52(18).