Supporting Information for:

# Exploring the Mechanism of the Hydroboration of Alkenes by Amine-Boranes Catalysed by [Rh(Xantphos)]$^+$

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## Crystallography

Relevant details about structure refinement are given in Table S-1. Data were collected on a Enraf Nonious Kappa CCD difractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low temperature device; data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[1] The structures were solved using SIR92[2] and refined using CRYSTALS.[3]

In both **3** and **8**, the difference map indicated the presence of diffuse electron density believed to be disordered pentane solvent. SQUEEZE[4, 5] was used in each, leaving a void from which the electron density was removed. Rotational disorder of some of the $CF_3$ groups of the anion in both **3** and **8** was treated by modelling the fluorine atoms over two sites and restraining their geometry. The hydrogen atoms were found on the Fourier map and refined before RIDE restraints were added.

In **3**, H11 and H12 ride on B1. Furthermore, rotational disorder of the $NMe_3$ group was treated similarly to the $CF_3$ groups, and disorder of the $BCH_2CH_2SiMe_3$ chain was treated by modelling over two sites and refining the occupancies.

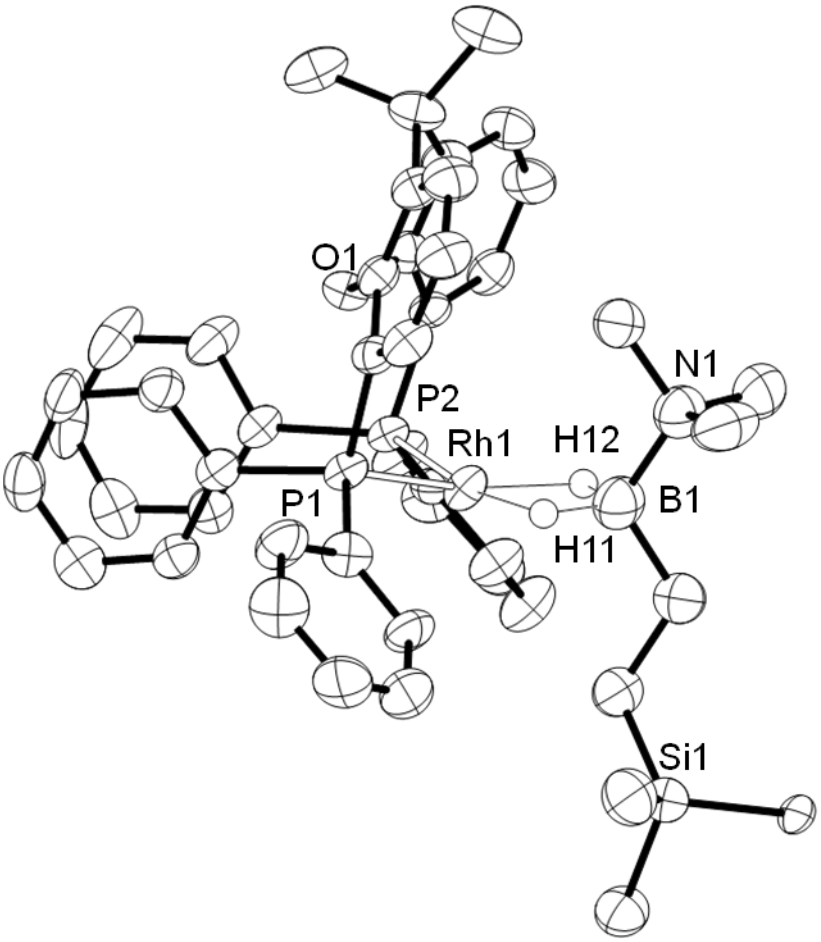


**Figure S-1** Complex **[3]**$^{+}$. Displacement ellipsoids are drawn at the 50% probability level. All carbon-bound H atoms omitted for clarity. Only one component of the disordered $NMe_3$ and $SiMe_3$ groups are shown. Selected bond lengths (Å) and angles (˚): Rh1-P1, 2.2397(17); Rh1-P2, 2.2675(16); Rh1-O1, 3.2338(73); Rh1-B1, 2.187(7); B1-N1, 1.595(4); P1-Rh1-P2, 98.24(6); N1-B1-C93, 113.3(4).

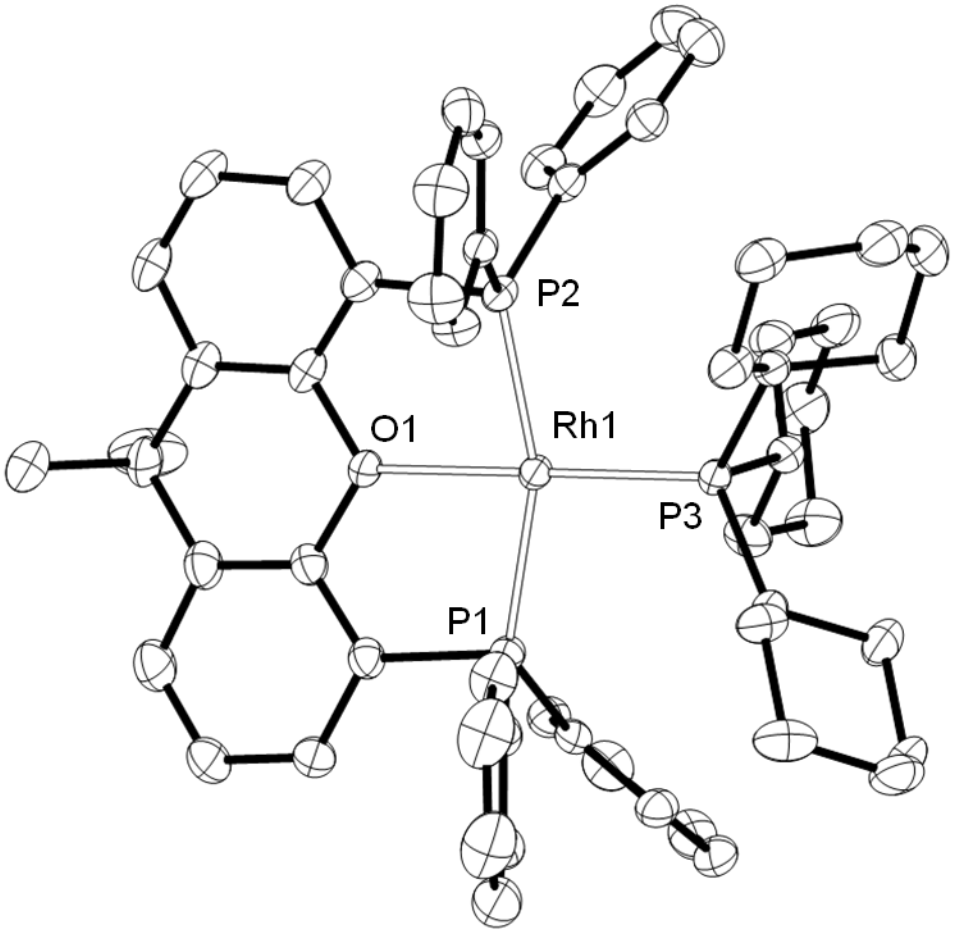


**Figure S-2** Complex **[8]**$^{+}$. Displacement ellipsoids are drawn at the 50% probability level. H atoms omitted for clarity. Selected bond lengths (Å) and angles (˚): Rh1-P1, 2.2854(7); Rh1-P2, 2.2923(7); Rh1-O1, 2.2395(19); Rh1-P3, 2.2611(7); P1-Rh1-P2, 159.70(3); O1-Rh1-P3, 170.44(6).

**Table S-1** Selected crystallographic data for **3** and **8**

| | **3** | **8** |
|---|---|---|
| CCDC number | 1001382 | 1001383 |
| Formula | $C_{79}H_{68}B_2F_{24}NOP_2RhSi$ | $C_{89}H_{77}BF_{24}NOP_3Rh$ |
| *M* | 1717.93 | 1825.18 |
| Crystal System | Triclinic | Triclinic |
| Space group | P -1 | P -1 |
| *T* [K] | 150(2) | 150(2) |
| *a* [Å] | 16.6243(5) | 12.90760(10) |
| *b* [Å] | 16.8939(5) | 17.8030(2) |
| *c* [Å] | 17.7667(7) | 19.9590(3) |
| *α* [deg] | 110.6501(11) | 87.9991(5) |
| *β* [deg] | 107.1873(12) | 74.6948(5) |
| *γ* [deg] | 106.290(2) | 87.0039(6) |
| *V* [Å$^3$] | 4026.5(3) | 4416.68(9) |
| *Z* | 2 | 2 |
| Density [gcm$^{-3}$] | 1.417 | 1.372 |
| *μ* [mm$^{-1}$] | 0.366 | 0.343 |
| *θ* range [deg] | 5.113 ≤ θ ≤ 25.018 | 5.099 ≤ θ ≤ 27.491 |
| Reflns collected | 36954 | 61434 |
| $R_{int}$ | 0.078 | 0.050 |
| Completeness | 98.7% | 98.8% |
| Data/restr/param | 11566/ 2846/ 1186 | 20022/ 456/ 1128 |
| $R_1$ [I > 2σ(I)] | 0.0860 | 0.0510 |
| $wR_2$ [all data] | 0.2043 | 0.1393 |
| *GoF* | 0.9482 | 0.9426 |
| Largest diff. pk and hole [eÅ$^{-3}$] | 3.32, -1.68 | 1.18, -0.85 |

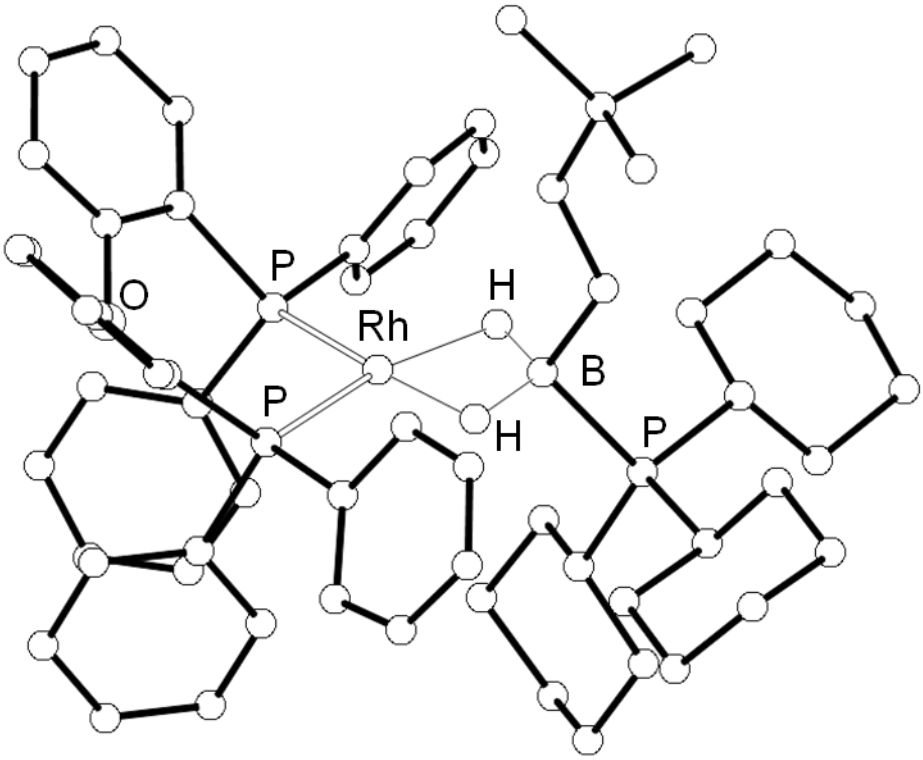


**Figure S-3** Ball and stick representation of a partially refined structure of **7**. Hydrogen atoms placed in calculated positions. The $[BAr^F{}_4]^-$ anion and all carbon-bound H atoms omitted for clarity. The X-ray data is of poor quality so the structure is presented for connectivity purposes only. Selected crystallographic data: Trinclinic, P-1, *a* = 18.0544(7) Å, *b* = 23.5573(10) Å, *c* = 28.2957(12) Å, *α* = 100.4469(17)˚, *β* = 90.0292(19)˚, *γ* = 112.4783(19)˚, *V* = 10903.5(8) Å$^3$.

## References


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