Thermal rearrangement mechanisms in icosahedral carboranes and metallocarboranes.

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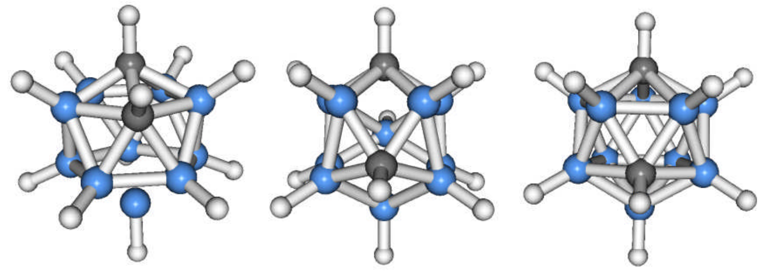
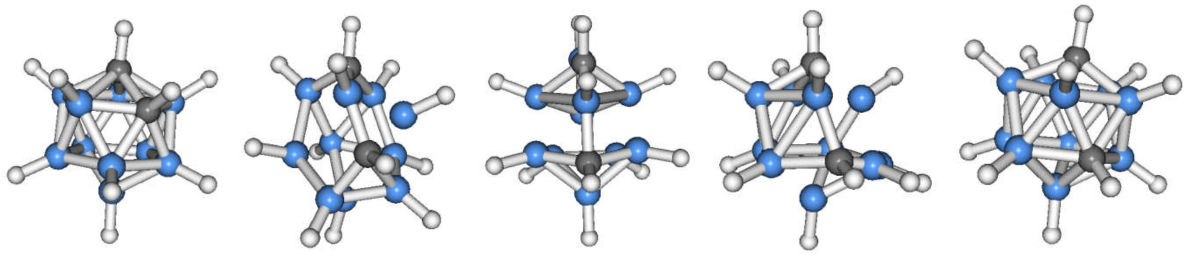
Supporting Information

TFR structures



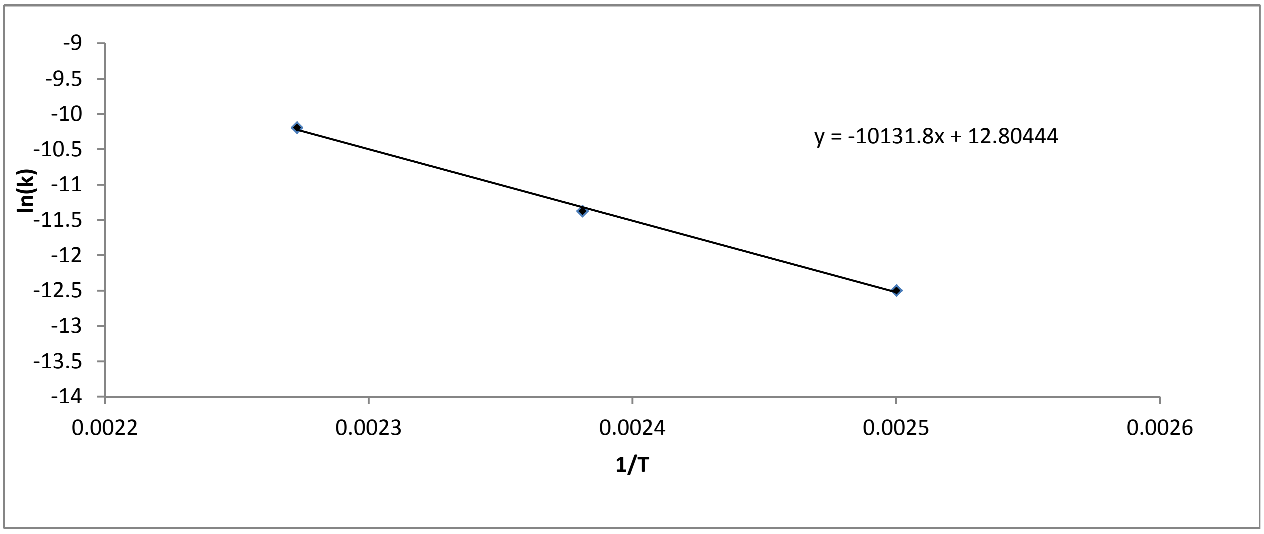
Ortho-carborane TFR-TS *Meta*-carborane

non-TFR structures



Ortho-carborane NON-TS1 NON-INT NON-TS2 *Meta*-carborane

Fig. S1 Structures of carborane species from the TFR and non-TFR rearrangement pathways



"Samples of isotopically normal *o*-carborane were heated at 400, 420, and 440˚C. The rate of isomerisation of o-carborane to m-carborane for these samples was determined from the relative integrals of the ^{11}B NMR resonances of *o*- and *m*-carborane. The rate of isomerisation was (3.73±0.15) x 10^{-6} s^{-1}, (1.15±0.05) x $l0^{5}$ $\mathbf{s^{-1}}$**,** and (3.74±0.15) x s-l at 400, 420, and 440˚C, respectively. Activation parameters for the isomerisation are ΔG* = 57.3±0.4 kcal mol^{-1}, Δ*H** = 54±15 kcal mol^{-1}, and ΔS* = -5±11 cal mol^{-1} K^{-1}, which are in close agreement with earlier studies"

Fig. S2 Rate constant derivation for *ortho-meta* carborane rearrangement, with explanatory text from Ref [11]

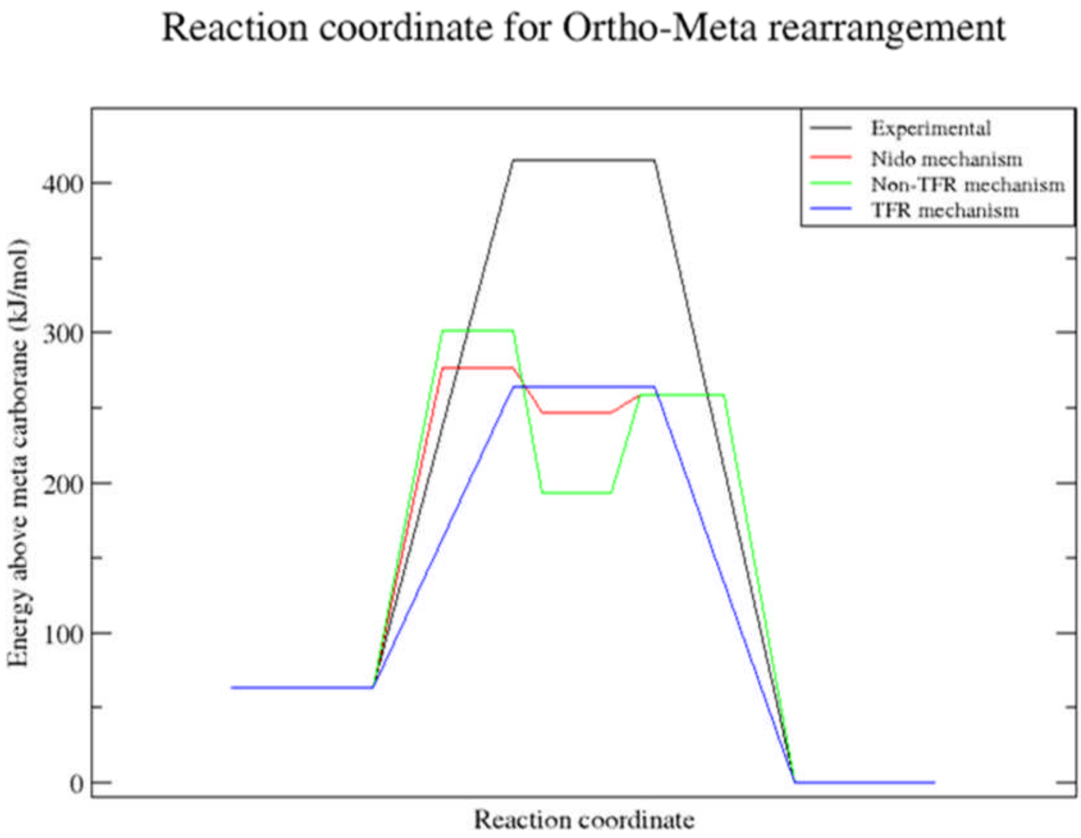
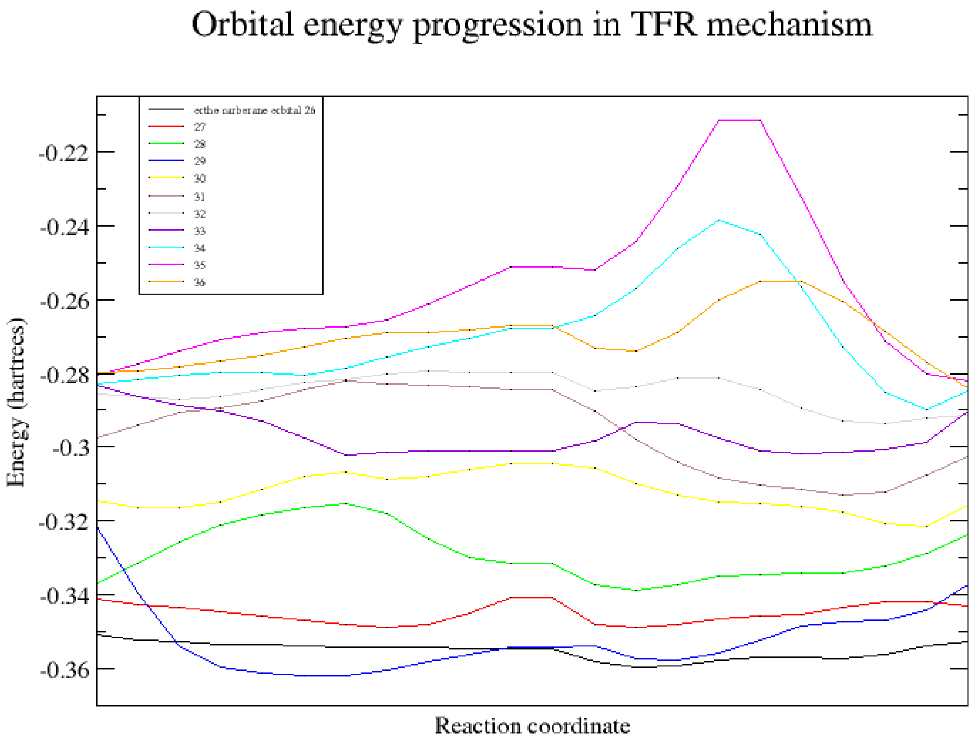
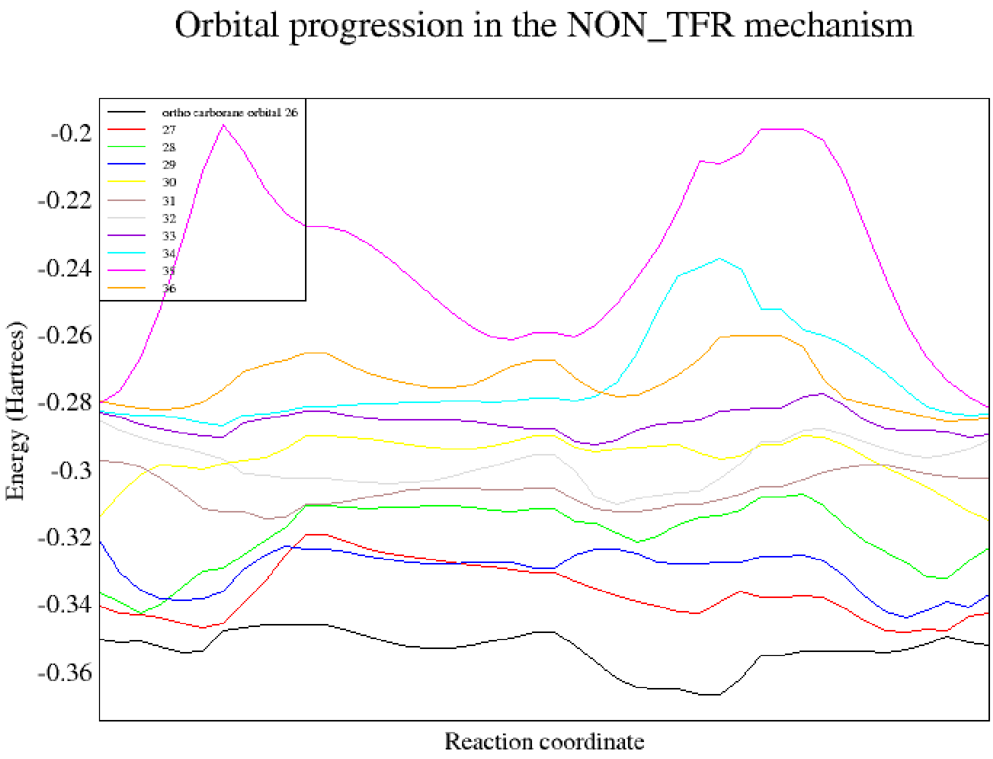


Fig. S3 Total energy profiles for the three different mechanisms for *ortho-meta* rearrangement, plotted together with the experimentally-derived activation energy. *Ortho* is at the extreme left of the reaction coordinate, *meta* at the right.

TFR 10 highest energy orbital progression



NON-TFR 10 highest energy orbital progression



Nido 10 highest energy orbital progression

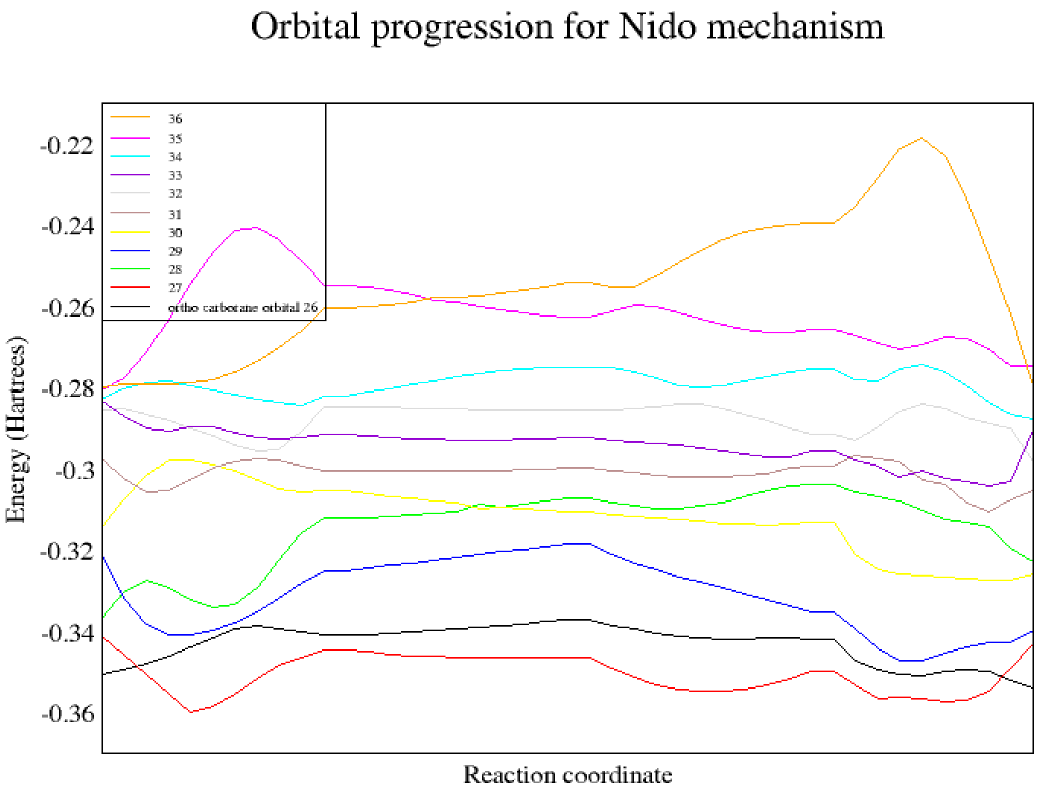
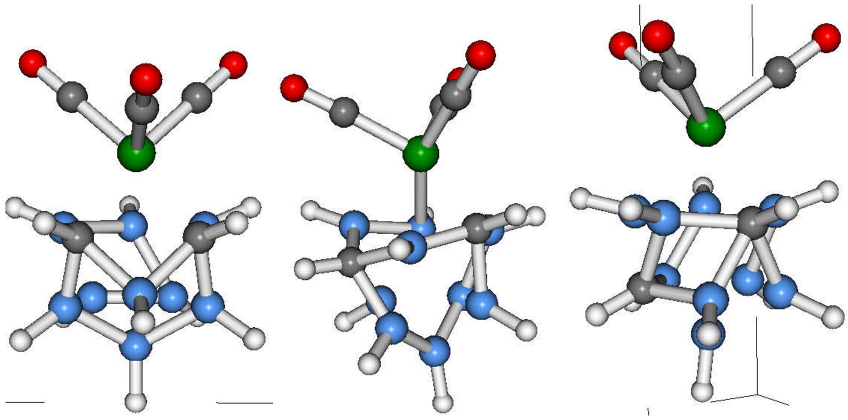
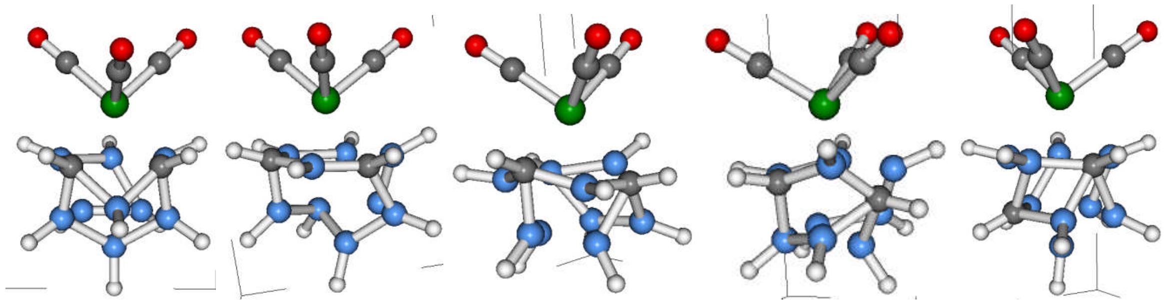


Fig. S4 Orbital energy progressions for carborane complexes for three possible mechanisms for *ortho-meta* rearrangement. In each case, *ortho* is at the extreme left of the reaction coordinate, *meta* at the right. For images of orbital progressions, contact authors.



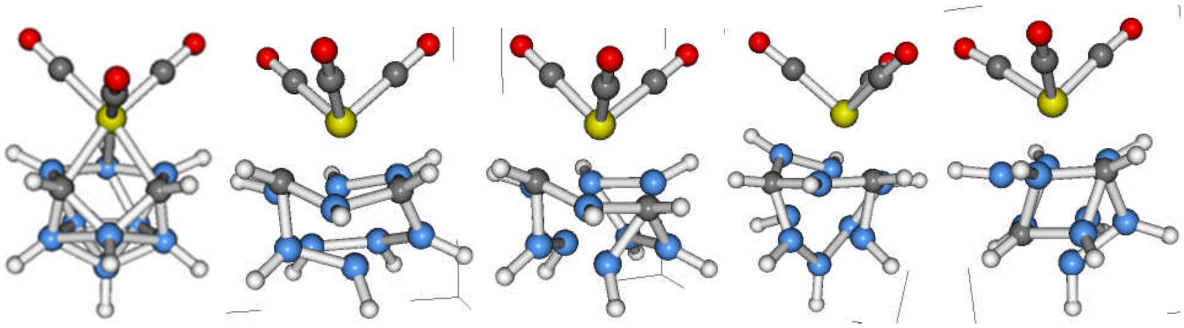
Ortho TS1 Meta

Technetium TFR structures



Ortho TS1 INT TS2 Meta

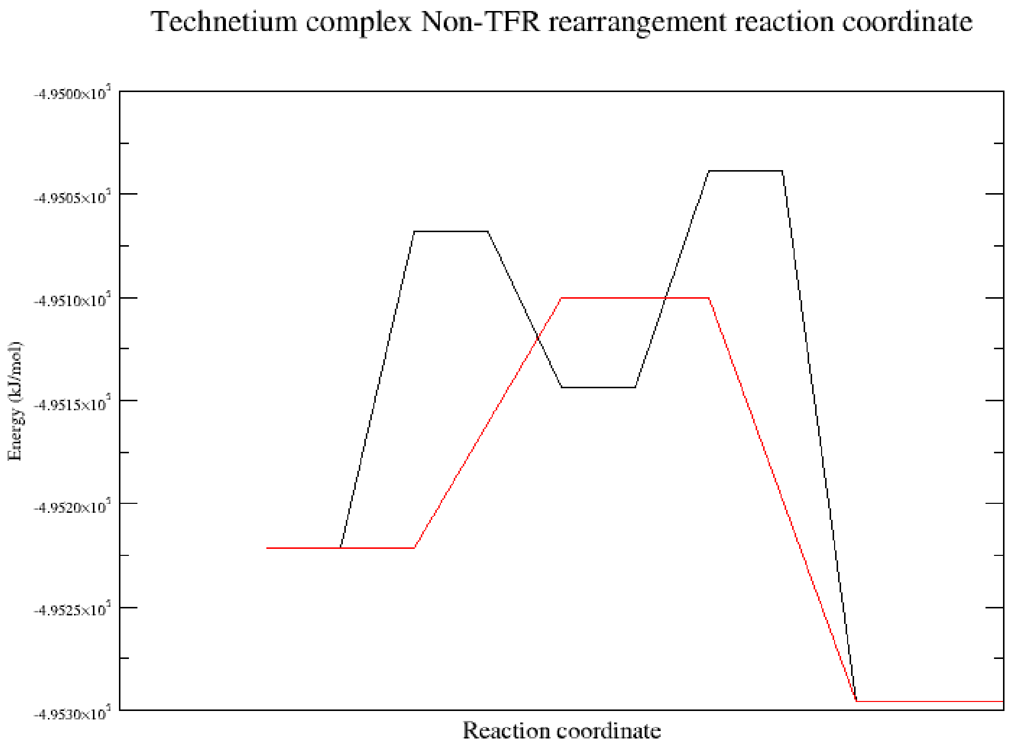
Technetium NON-TFR structures



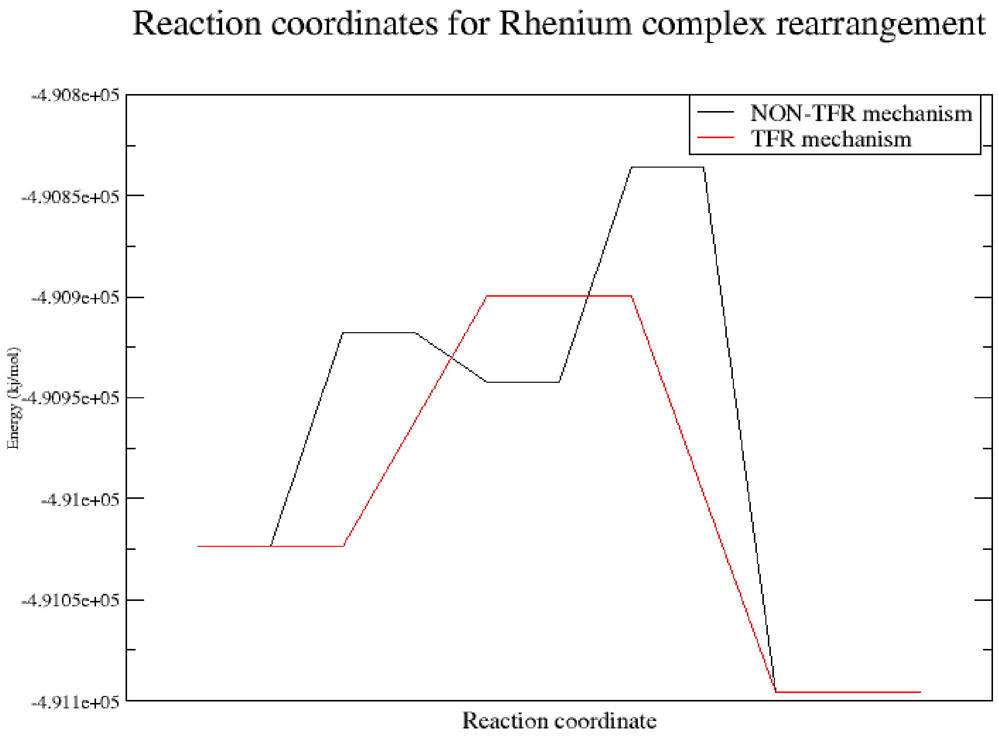
Ortho TS1 INT TS2 Meta

Rhenium NON-TFR structures

Fig. S5 Key structures in metal-carborane complex rearrangements



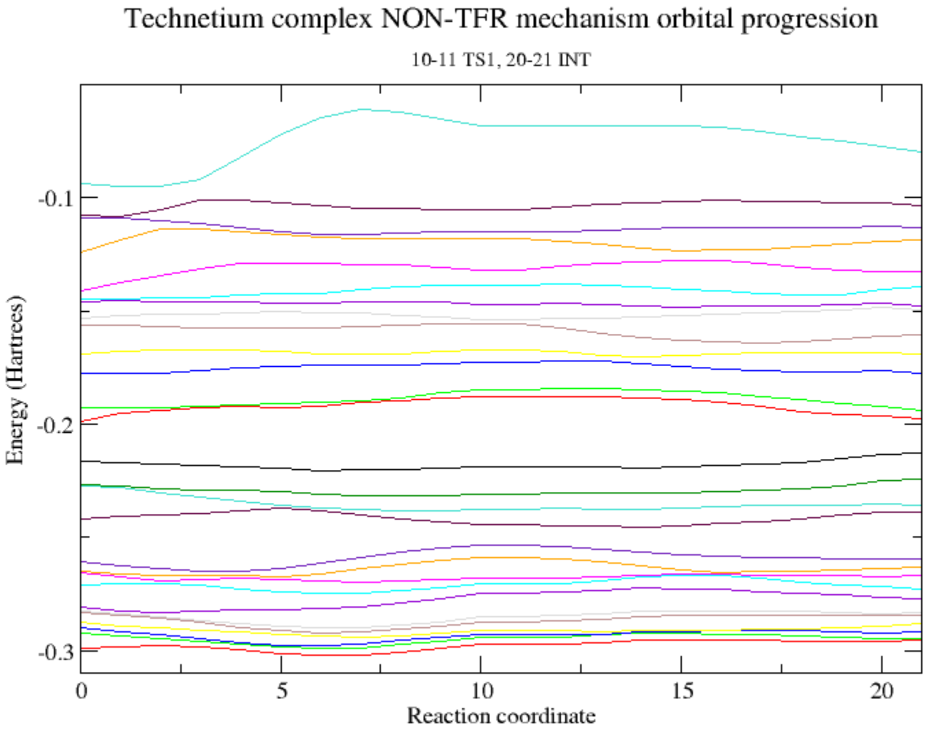
Technetium complex rearrangements. Red line is TFR, black line is Non-TFR reaction coordinate.



Rhenium complex rearrangements

Fig. S6 Reaction coordinates for metal-complexes

Technetium complex NON-TFR rearrangement



Rhenium complex NON-TFR rearrangement

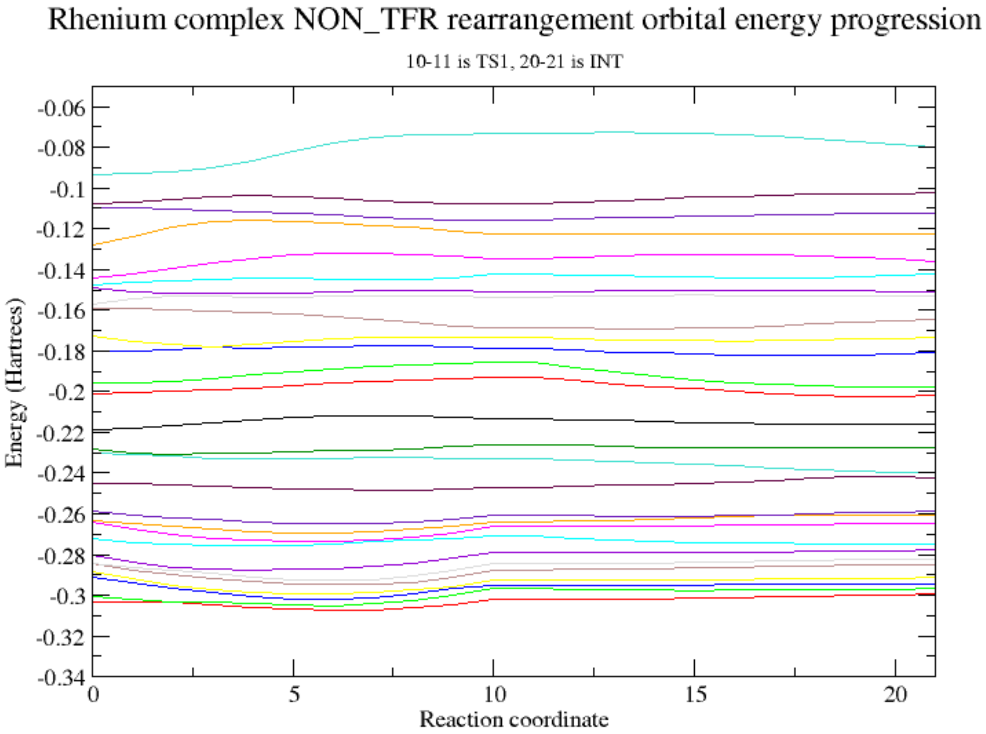


Fig. S7 Orbital energy progression for metal complexes' NON-TFR *ortho-meta* rearrangements. For images of orbital progression, contact authors

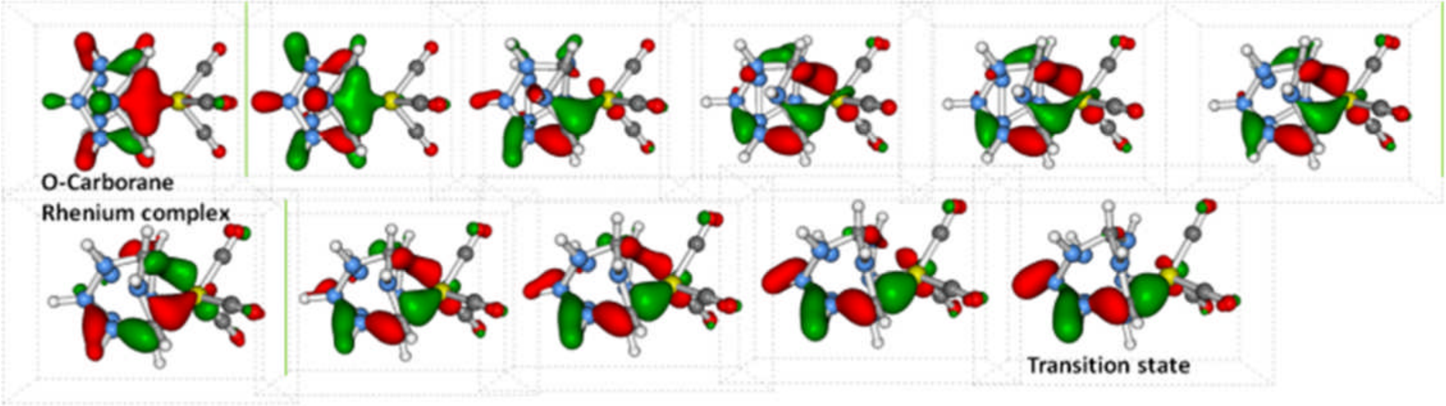


Fig. S8 The progression of orbital HOMO-8 from *ortho* to TS rhenium carborane complex, in the TFR mechanism.