A mechanistic exploration of the Wilkinson hydrogenation catalyst. Part 1: Model templates

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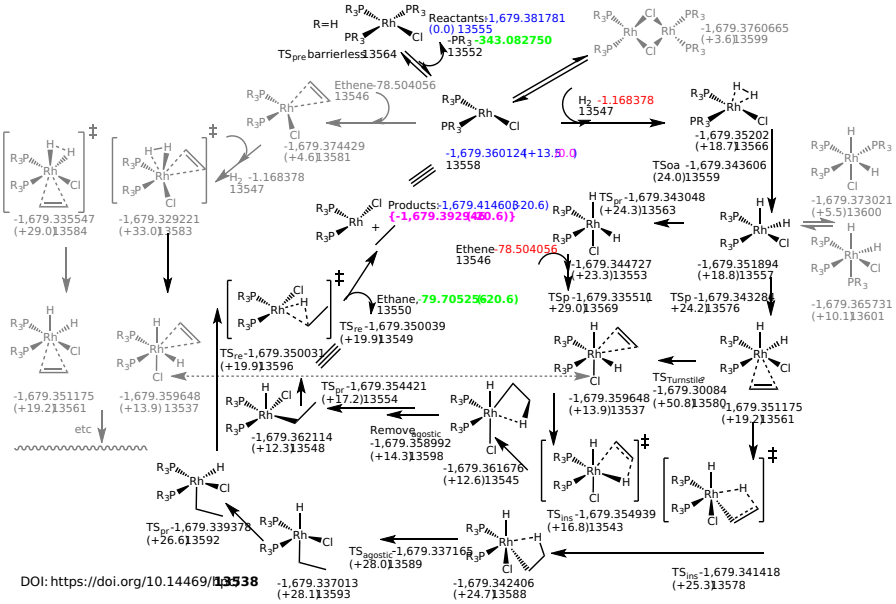

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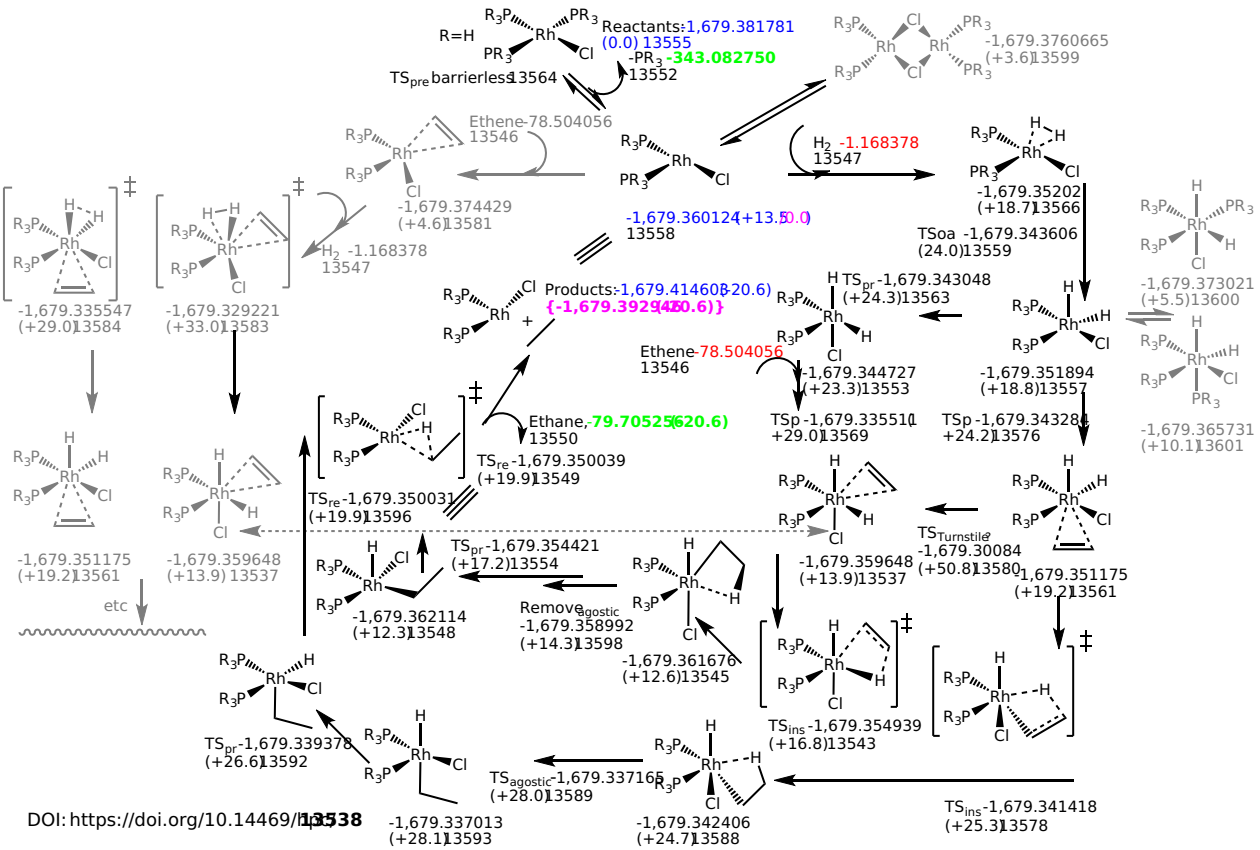
Geoffrey Wilkinson first reported his famous work on the hydrogenation catalyst that now bears his name in 1965[cite]10.1039/C19650000131[/cite] and I met him at Imperial College around 1969 and again when I returned there in 1977. He was still working on these catalysts then and I was privileged to collaborate with him on unravelling the NMR spectra of some of these compounds. [cite]10.1039/C39820000482[/cite],[cite]10.1016/S0277-5387(00)86558-4[/cite], [cite]10.1016/0277-5387(82)80008-9[/cite]. During that period, computational modelling of the mechanisms of molecules containing transition elements was still in its infancy and I never extended my collaboration into this area at that time. Now, even if belatedly, I decided to explore this aspect and started to do this about two weeks ago. Here I thought that I would use this opportunity to show how I am going about it.

The diagram below is an extension of the one found at Wikipedia and here is acting in effect as a "Finding Aid" for the data that would be gradually generated for the mechanism. At the outset, I decided to build my own version to also act as a laboratory notebook charting my progress, building the finding aid as I went. This explains, by the way the rather amorphous expansion of the diagram!



Before discussing the mechanism itself, I point out some features of the diagram itself. Each computed species is associated with a free energy (in Hartree) acting as a FAIR-type identifier for the calculation[cite]10.59350/nk414-18p76[/cite] as a means of improving the findability of the data and the replicability of the result. Also included is the energy relative to the lowest point in the mechanism (itself set to 0.0) and next to that you can see a five digit code. If prefixed by the string `https://doi.org/10.14469/hpc/` this acts as a digital object identifier

(DOI) for each calculation, pointing to a landing page providing information about the archived dataset. The top-level DOI 13538 acts as a collection or container for the project, being also the DOI that would normally be cited in any description of the results, such as here. The diagram above uses the graphical vector format SVG, which allows hyperlinks to be inserted. So if you click on one of these strings embedded in the diagram (see e.g.[cite]10.1039/C7SC03595K[/cite]), it should take you straight to the data for that result.

The first point to make about the mechanism itself are the stereochemistries of the various 3-6 coordinate species, which in the Wikipedia mechanism are not really discussed. On the right hand side of the diagram, two alternative pathways with different stereochemistry are included. On the lhs (in grey) a different sequence of events is set out, which rejoins the main pathway at the dotted line. The next point to make is the level of computational theory adopted, it being the MN15L DFT procedure, which is suitable for transition metal elements, and the Def2-TZVPP basis set – together with a continuum solvent correction. For rapid exploration, I made an initial big approximation, which was to set the substituent on the phosphorus to R=H rather than R=Ph. This allows templates for the entire cycle to be constructed relatively rapidly, and then revisited as desired in a follow up exploration using these templates.

The mechanistic features are described below. The DOI suffix is quoted for you to locate on the diagram.

1. To the right of the cycle, we follow the accepted route, which is initial loss of one phosphine ligand, followed by insertion of H_2 onto the Rhodium (13559)
2. The hydrogens inserted can pseudorotate into a different stereochemical orientation (13563) and either of these stereoisomers can now complex with the alkene (13569 or 13576).
3. The two resulting 6-coordinate complexes could in theory interconvert by a different pseudorotation (Turnstile[cite]10.1021/ic0519988[/cite]), but this appears high in energy (13580)
4. One of the carbons of the alkene complex now inserts into the Rh-H bond (13543, 13578) to form a Rh-alkyl complex in which an agostic-style Rh-H interaction is apparent (13545, 13588)
5. The agostic interaction is removed (13598, 13589) to form stereochemical isomers of the Rh-alkyl complex (13593)
6. Another pseudorotation sets up the stereochemistry for the final step (13554, 13592).
7. The remaining Rh-C bond can now insert into the remaining Rh-H bond, at which point the two separate isomeric paths now coalesce to form a single transition state (13596 ≡ 13549) releasing the activated Rh complex where the cycle first started and hence completing the cycle.
8. To the right of the diagram are two cul-de-sac intermediates (in grey) which result from re-addition of phosphine to the hydride complex.
9. To the left of the diagram is an alternative sequence which involves adding alkene to the Rh first, and only then followed by H_2 addition (13584, 13583). The energies of this path does appear significantly higher than the alternative. Once the alkene/H_2 complex is

formed, it now rejoins the cycle on the right of the diagram (horizontal double headed dashed arrow).

You can follow the (relative) energies of this mechanism from the diagram; they are all reasonable for a thermal reaction. However, I will refrain from making any overall decision about the rate determining step (thought to be step 7 above), because the model for both the phosphine ligand and the (unsubstituted) alkene do not yet have any steric components, which are known to be important. What we have here therefore are templates for the next stage of studying the mechanism, when Ph_3P and e.g. propene will replace the current models.

Here I have tried to show a somewhat different approach to "laboratory notebook management", whereby each step in the investigation can be accompanied by a persistent identifier (as a DOI) to that step, pointing to a location where the coordinates for the template can be readily obtained. The DOIs are added as each step completes, in this case into a Chemdraw diagram. Unfortunately, Chemdraw does not have a hyperlink tool (I did ask them to a few years back) and this can only be added to the export SVG file at the final stage. I inserted 40 such hyperlinks using a text editor; the process was not too onerous and because the SVG file is text based, it is also easily edited for errors and small corrections. Curiously, SVG editing tools such as the veritable Inkscape do not currently support addition of hyperlinks and given the well-established mechanisms for hyperlinking text, it seems odd that this has not developed for images.