Computational Part

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1. Computational Methods

Density functional theory (DFT) was used to elucidate the mechanism of the Ru(II) catalyzed hydrogenation of alkynes. All geometry optimizations were performed using the M06\(^1\) functional. The triple-\(\zeta\) quality def2-TZVP\(^2\) basis set was used for all atoms. The 28 inner-shell core electrons of the ruthenium atom were described by the corresponding def2 effective core potential\(^3\) accounting for scalar relativistic effects (def2-ecp).

Stationary points were characterized by evaluating the harmonic vibrational frequencies at the optimized geometries. Zero-point vibrational energies (ZPVE) were computed from the corresponding harmonic vibrational frequencies without scaling. Relative free energies (\(\Delta G\)) were determined at standard pressure (1 bar) and at room temperature (298 K). The thermal and entropic contributions were evaluated within the rigid-rotor harmonic-oscillator approximation. Solvation contributions were included for dichloromethane on the optimized gas-phase geometries employing the SMD solvation model\(^4\) using the same functional and basis set. All calculations were performed using Gaussian09 with the ultrafine grid.\(^5\)

2. Hydrogenation of 2-butyne using the neutral ruthenium catalyst: Description of additional pathways

Hydrogenation has experimentally been shown to lead to the formation of side products. The pathways involved are discussed here in some detail.

The association of H\(_2\) to C\(_2\) is uphill in Gibbs free energy by 11.3 kcal/mol (Scheme S1). From the association complex R\(_1\), oxidative addition of hydrogen affords the dihydride R\(_2\) which readily delivers a hydride to the \(\alpha\)-carbon forming R\(_3\) which exhibits an \(\alpha\)-agostic interaction.

Intermediate R\(_3\) can undergo facile rotation about the Ru-C bond to enable agostic interactions with either hydrogen at the \(\beta\) position (Scheme S2). The barrier is negligible for formation of an agostic interaction with a primary hydrogen of the methyl group (TS\(_{R3-D1}\)) affording D\(_1\) which can undergo \(\beta\)-hydride elimination with a low barrier (TS\(_{D1-D2}\), 3.7 kcal/mol); from the resulting complex D\(_2\), molecular hydrogen H\(_2\) can easily be extruded. An alternative low-energy rotation about the Ru-C bond transforms R\(_3\) into B\(_1\) showing an agostic interaction with a secondary hydrogen of the ethyl group (via TS\(_{R3-B1}\), 2.1 kcal/mol).
Scheme S1. Detailed mechanism for the addition of H₂ to C₂ from the side of the methyl group. Values in parenthesis are Gibbs free energies in units of kcal·mol⁻¹.

Intermediate B₁ exhibits a strong preference for Ru-H reductive elimination to form the saturated product B₂ rather than β-hydride elimination. By contrast, Ru-H reductive elimination from D₁ is hampered by a less favorable alignment as compared with that in B₁.

Scheme S2. Detailed mechanism for the conversion of R₃ to the saturated (B₂) and isomerized (D₄) products. Values in parenthesis are Gibbs free energies in units of kcal·mol⁻¹.
We also studied the approach of molecular hydrogen from the side of the ethyl group (Schemes S3 and S4). The computed Gibbs free energy profile is shown in Figure S1. The landscape is very similar to that obtained for the approach from the side of the methyl group (see Scheme 3 of the main paper). The approach from the ethyl side yields the saturated alkane $B_2'$ and the desired $E$-alkene ($E_2$) while the approach from the methyl side leads to the isomerized product ($D_4$) and the saturated alkane.

**Figure S1.** Gibbs free energy profile for addition of $H_2$ to $C_2$ from the side of the ethyl group.

**Scheme S3.** Detailed mechanism for the addition of $H_2$ to $C_2$ from the side of the ethyl group. Values in parenthesis are Gibbs free energies in units of kcal mol$^{-1}$. 

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S4
Scheme S4. Detailed mechanism for the conversion of \( \text{R3}' \) to the saturated alkane (\( \text{B2}' \)) and the \textit{trans}-alkene (\( \text{E2} \)) products. Values in parenthesis are Gibbs free energies in units of kcal·mol\(^{-1}\).

There are two further pathways from \( \text{C2} \) that have not yet been discussed in detail, namely direct formation of \textit{trans}-alkene \( \text{E2} \) and isomerization in the absence of \( \text{H}_2 \). The corresponding Gibbs free energy profiles are displayed in Figure S2. The direct 1,2-hydrogen transfer exhibits the highest barrier of any process investigated presently and is thus unlikely to happen to any measurable extent. The isomerization from \( \text{C2} \) to \( \text{D4} \) involves an initial primary \( \beta \)-hydrogen abstraction by \( \text{Ru} \) from the methyl group. The computed overall barrier is similar to that for formation of the \textit{cis}-alkene \( \text{Z3} \) (compare \( \text{TS}_{\text{Z1-Z2}} \) with \( \text{TS}_{\text{Z1-Z2}} \)). Alternative pathways involving molecular hydrogen remain energetically most favorable and will thus be more likely.
Figure S2. Gibbs free energy profile (in units of kcal mol\(^{-1}\)) for direct formation of E2 from C2 and for isomerization in the absence of H\(_2\).

3. Hydrogenation of the alkyne substrate (8b) using the neutral ruthenium catalyst

After the thorough study of all mechanistic pathways for the model substrate 2-butynel using the neutral ruthenium(II) catalyst, we computed selected pathways for the actual substrate 8b using the same neutral ruthenium catalyst. These pathways are indicated in Schemes S5 and S6. The key results are: (1) The Gibbs free energy barrier for hydride transfer (via TS\(_{A2-A3}\)) is lowered by 8 kcal mol\(^{-1}\) compared to the model substrate. This lowering most probably arises from the hydrogen bonding interaction between the hydroxyl group and the chloride ligand. (2) The formation of carbene C2 from E1 is preferred by 2.6 kcal mol\(^{-1}\) over the competing path that directly leads to E-alkene. Therefore, C2 should mostly be formed from E1. (3) In the E1→C2 conversion, an intermediate similar to C1 (for the model substrate) does not exist. (4) C2 may adopt a less stable conformation, in which the methoxy group is not coordinated to the Ru center; this destabilizes the carbene C2' by 6.6 kcal mol\(^{-1}\) relative to C2. (5) All the paths originating from C2 have high energy barriers (in kcal mol\(^{-1}\)): TS\(_{E1-E2}\) (26.6), TS\(_{C2-E2}\) (31.5), and TS\(_{R1'-R3'}\) (38.6). Therefore, the highly stable carbene C2 acts as a thermodynamic sink in this reaction.
These results are in full agreement with the experimental finding that only C2 is formed when using the actual substrate 8b with the neutral ruthenium catalyst.

Scheme S5. Formation of the metallacyclic complex E1. Hydrogen bonding interactions are shown in red. Gibbs free energies in kcal mol$^{-1}$ are relative to the initial adduct.

Scheme S6. Pathways from E1 leading to either E-alkene or alkane. Hydrogen bonding interactions are shown in red. Gibbs free energies in kcal mol$^{-1}$ are relative to the initial adduct.
4. Hydrogenation of 2-butyne using the cationic ruthenium catalyst

We also considered the cationic catalyst [Cp*Ru(CH$_3$CN)$_3$]$^+$, in place of the neutral catalyst, to study the change in reactivity towards hydrogenation of 2-butyne (see Figures S3 – S5). We use the same labeling scheme as in the neutral case. Here, we only pinpoint key reactivity differences. In the cationic case, A1 undergoes H$_2$ activation and C-H bond formation in a concerted manner via TS$_{A1-A3}$ to yield A3, whereas the reaction is stepwise in the neutral case (Figure S3). Moreover, the formation of A3 is more facile in the cationic case due to a reduced barrier of 22.9 kcal mol$^{-1}$, compared with 27.8 kcal mol$^{-1}$ in the neutral case. Intermediate C2 is less stable than in the neutral case. The reaction between C2 and H$_2$ again involves a concerted H$_2$ activation and C-H bond formation (via TS$_{R1-R3}$/TS$_{R1'-R3'}$), which is different from the stepwise process in the neutral case (Figure S4). C2 is more easily hydrogenated than in the neutral case by 6.0 kcal mol$^{-1}$. Other than this, we find no major differences.

**Figure S3.** Gibbs free energy profile (in units of kcal-mol$^{-1}$) for the hydrogenation of 2-butyne with the cationic catalyst.
Figure S4. Gibbs free energy profile (in units of kcal·mol⁻¹) for the reaction of carbene C2 with H₂ in the case of the cationic catalyst. H₂ may approach either from the ethyl or methyl side. Primed (unprimed) labels denote the H₂ addition from the ethyl (methyl) side.

Figure S5. Gibbs free energy profile (in units of kcal·mol⁻¹) for direct formation of E2 from C2 and isomerization in the absence of H₂ (in the case of the cationic catalyst).
5. Energy table for the reaction of the model substrate (2-butyne) with the neutral Ru(II) catalyst

Table S1. Listed are the SCF energy, zero point vibrational energy (ZPVE), enthalpy correction (H corr), and Gibbs free energy correction (G corr) determined on the gas-phase geometries for all stationary points calculated using the neutral Ru catalyst with the 2-butyne substrate. The single imaginary frequency (υi cm\(^{-1}\)) is also listed for all transition states. Single point solvent (DCM) corrected SCF energies on the gas phase geometries are also documented. All energies are in atomic units.

|        | SCF gas | SCF DCM | ZPVE   | H corr | G corr | υi (cm\(^{-1}\)) |
|--------|---------|---------|--------|--------|--------|-----------------|
| H\(_2\) | -1.170676 | -1.170379 | 0.009802 | 0.013160 | -0.001642 |                |
| COD\(^e\) | -311.885137 | -311.895992 | 0.179556 | 0.187981 | 0.148036 |                |
| 2-butyne | -155.909153 | -155.916818 | 0.084023 | 0.090553 | 0.054557 |                |
| A0      | -1257.045711 | -1257.069358 | 0.405931 | 0.429301 | 0.357267 |                |
| A1      | -1102.221195 | -1102.244527 | 0.325399 | 0.348672 | 0.275921 |                |
| TS\(_{A1-A2}\) | -1102.210663 | -1102.233644 | 0.323785 | 0.346078 | 0.276381 | i242            |
| A2      | -1102.212742 | -1102.235656 | 0.325984 | 0.348381 | 0.278153 |                |
| TS\(_{A2-A3}\) | -1102.205382 | -1102.229081 | 0.323508 | 0.345889 | 0.275004 | i460            |
| A3      | -1102.215509 | -1102.241864 | 0.327269 | 0.349804 | 0.278601 |                |
| TS\(_{A3-E1}\) | -1102.215400 | -1102.242330 | 0.327108 | 0.348993 | 0.279117 | i31             |
| E1      | -1102.231583 | -1102.254222 | 0.328121 | 0.350319 | 0.279811 |                |
| TS\(_{E1-E2}\) | -1102.223233 | -1102.245404 | 0.327278 | 0.348907 | 0.279170 | i37             |
| E2      | -1102.287611 | -1102.312147 | 0.332766 | 0.354917 | 0.284219 |                |
| TS\(_{E1-C1}\) | -1102.220078 | -1102.243464 | 0.327047 | 0.348985 | 0.279224 | i644            |
| C1      | -1102.223333 | -1102.246574 | 0.327793 | 0.350302 | 0.278611 |                |
| TS\(_{C1-C2}\) | -1102.221485 | -1102.244794 | 0.326783 | 0.348953 | 0.277775 | i449            |
| C2      | -1102.252791 | -1102.278138 | 0.331010 | 0.353699 | 0.280593 |                |
| TS\(_{C2-Z1}\) | -1102.225181 | -1102.249585 | 0.327354 | 0.349208 | 0.279344 | i557            |
| Z1      | -1102.228292 | -1102.252327 | 0.328087 | 0.350438 | 0.279260 |                |
| TS\(_{Z1-Z2}\) | -1102.217448 | -1102.240521 | 0.327720 | 0.349334 | 0.280024 | i44             |
| Z2      | -1102.226201 | -1102.248598 | 0.327958 | 0.350338 | 0.279233 |                |
| TS\(_{Z2-Z3}\) | -1102.224513 | -1102.246874 | 0.326795 | 0.348798 | 0.278856 | i481            |
| Z3      | -1102.284838 | -1102.309165 | 0.330349 | 0.355035 | 0.285069 |                |
| TS\(_{A3-Z1}\) | -1102.210127 | -1102.237070 | 0.327045 | 0.348885 | 0.279276 | i179            |
| TS\(_{C2-R1}\) | -1103.420214 | -1103.444479 | 0.344606 | 0.368439 | 0.294651 | i215            |
| R1      | -1103.428659 | -1103.451036 | 0.348876 | 0.372025 | 0.299383 |                |
| TS\(_{R1-R2}\) | -1103.419613 | -1103.441294 | 0.347725 | 0.369841 | 0.299586 | i33             |
| R2      | -1103.419820 | -1103.441285 | 0.348038 | 0.370895 | 0.298507 |                |
| TS\(_{R2-R3}\) | -1103.417505 | -1103.439549 | 0.346722 | 0.369267 | 0.297909 | i470            |
| R3      | -1103.430921 | -1103.455571 | 0.351464 | 0.373784 | 0.302813 |                |
| TS\(_{R3-D1}\) | -1103.425875 | -1103.455841 | 0.351174 | 0.373233 | 0.303033 | i89             |
| D1      | -1103.451315 | -1103.476033 | 0.352164 | 0.374262 | 0.304014 |                |
| TS\(_{D1-D2}\) | -1103.444955 | -1103.467209 | 0.348903 | 0.370770 | 0.301143 | i487            |
6. Energy table for the reaction of the substrate (8b) with the neutral Ru(II) catalyst

Table S2. Listed are the SCF energy, zero point vibrational energy (ZPVE), enthalpy correction \( (H_{\text{corr}}) \), and Gibbs free energy correction \( (G_{\text{corr}}) \) computed on the gas-phase geometries from Schemes S5 and S6. Single imaginary frequencies \( (\nu_i \text{ cm}^{-1}) \) are also listed for all transition states. Single point solvent (DCM) corrected SCF energies on the gas phase geometries are also documented. All energies are in atomic units.

|          | SCF\(_{\text{gas}}\) | SCF\(_{\text{DCM}}\) | ZPVE  | \( H_{\text{corr}} \) | \( G_{\text{corr}} \) | \( \nu_i \text{ cm}^{-1} \) |
|----------|---------------------|---------------------|-------|------------------------|------------------------|----------------|----------|
| \( \text{H}_2 \) | -1.170676           | -1.170379           | 0.009802 | 0.013160               | -0.001642           | \( \text{not applicable} \) |
| \( \text{COD} \)   | -311.885137         | -311.895992         | 0.179556 | 0.187981               | 0.328132           | \( \text{not applicable} \) |

\( ^a \) COD = 1,5-cyclooctadiene.
7. Energy table for the reaction of the model substrate (2-butyne) with the cationic Ru(II) catalyst

Table S3. Listed are the SCF energy, zero point vibrational energy (ZPVE), enthalpy correction ($H_{\text{corr}}$), and Gibbs free energy correction ($G_{\text{corr}}$) computed on the gas-phase geometries from Figures S3, S4, and S5. Single imaginary frequencies ($\nu_i$ cm$^{-1}$) are also listed for all transition states. Single point solvent (DCM) corrected SCF energies on the gas phase geometries are also documented. All energies are in atomic units.

| Substrate | SCF$_{\text{gas}}$ | SCF$_{\text{DCM}}$ | ZPVE | $H_{\text{corr}}$ | $G_{\text{corr}}$ | $\nu_i$ (cm$^{-1}$) |
|-----------|-------------------|-------------------|-------|-------------------|-------------------|-------------------|
| H$_2$     | -1.170676         | -1.170379         | 0.009802 | 0.013160         | -0.001642        | i648              |
| CH$_3$CN  | -132.709408       | -132.719151       | 0.045207 | 0.049731         | 0.021232         |                  |
| Substrate | -155.909153       | -155.916818       | 0.084023 | 0.090553         | 0.054557         |                  |
| A0        | -882.893965       | -882.966911       | 0.363915 | 0.392357         | 0.303341         |                  |
| A1        | -774.526044       | -774.599262       | 0.372269 | 0.398281         | 0.318301         |                  |
| TS$_{A1-A3}$ | -774.509312     | -774.581394       | 0.369200 | 0.394765         | 0.315863         | i648              |
| A3        | -774.520908       | -774.595117       | 0.373835 | 0.399315         | 0.320423         |                  |
| TS$_{A3-E1}$ | -774.520894     | -774.595966       | 0.373519 | 0.398288         | 0.321125         | i51               |
| E1        | -774.530419       | -774.604269       | 0.374734 | 0.399891         | 0.321392         |                  |
| TS$_{E1-E2}$ | -774.520281     | -774.594635       | 0.373982 | 0.398637         | 0.321233         | i643              |
| E2        | -774.582284       | -774.659706       | 0.379505 | 0.404424         | 0.326956         |                  |
| TS$_{E1-C1}$ | -774.519668     | -774.593589       | 0.373391 | 0.398156         | 0.319854         | i69               |
| C1        | -774.523392       | -774.597224       | 0.375048 | 0.399966         | 0.323069         |                  |
| TS$_{C1-C2}$ | -774.521506     | -774.594664       | 0.373443 | 0.398393         | 0.320599         | i425              |
| C2        | -774.546072       | -774.621932       | 0.377198 | 0.402851         | 0.322441         |                  |
| TS$_{C2-Z1}$ | -774.525462     | -774.598846       | 0.373699 | 0.398463         | 0.321099         | i607              |
| Z1        | -774.529181       | -774.602270       | 0.374855 | 0.39986          | 0.322603         |                  |
| TS$_{Z1-Z2}$ | -774.515719     | -774.589987       | 0.373936 | 0.398451         | 0.321969         | i59               |
| Z2        | -774.523753       | -774.597899       | 0.374443 | 0.399758         | 0.321193         |                  |
|       | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} |
|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
|       | -774.522535 | -774.596607 | 0.373253   | 0.398274   | 0.320235   | i393       | -774.516821 | -774.591048 | 0.373486   | 0.398338   | 0.319774   | i157       |
| R1    | -775.729650 | -775.803949 | 0.394955   | 0.421201   | 0.340151   | i347       | -775.734265 | -775.810462 | 0.398205   | 0.423281   | 0.345756   | i93        |
| R3    | -775.728209 | -775.809622 | 0.397955   | 0.422697   | 0.345857   | i93        | -775.728209 | -775.809622 | 0.397955   | 0.422697   | 0.345857   | i93        |
| D1    | -775.754758 | -775.829239 | 0.399246   | 0.423958   | 0.347453   | i845       | -775.746630 | -775.820523 | 0.394944   | 0.419689   | 0.342982   | i845       |
| D3    | -775.75615  | -775.834197 | 0.396709   | 0.422502   | 0.343284   | i347       | -775.759802 | -775.833804 | 0.397811   | 0.423289   | 0.344855   | i93        |
| D4    | -775.719999 | -775.799535 | 0.397327   | 0.422607   | 0.344145   | i182       | -775.719999 | -775.799535 | 0.397327   | 0.422607   | 0.344145   | i182       |
| B1    | -775.759802 | -775.833804 | 0.397811   | 0.423289   | 0.344855   | i93        | -775.759409 | -775.833575 | 0.397595   | 0.422486   | 0.345126   | i387       |
| B2    | -775.782106 | -775.858228 | 0.401953   | 0.427617   | 0.347301   | i845       | -775.75615  | -775.834197 | 0.396709   | 0.422502   | 0.343284   | i845       |

|       | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} |
|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| R1    | -775.718051 | -775.794339 | 0.389638   | 0.417200   | 0.332020   | i117       | -774.506161 | -774.583579 | 0.373600   | 0.399089   | 0.318348   | i976       |
| R3'   | -775.728434 | -775.809782 | 0.398178   | 0.422840   | 0.346540   | i93        | -775.728434 | -775.809782 | 0.398178   | 0.422840   | 0.346540   | i93        |
| D1    | -775.755857 | -775.829754 | 0.398882   | 0.423720   | 0.344870   | i387       | -775.75615  | -775.834197 | 0.396709   | 0.421549   | 0.344014   | i178       |
| R3    | -775.728209 | -775.809622 | 0.397955   | 0.422697   | 0.345857   | i93        | -775.759054 | -775.833791 | 0.397325   | 0.422305   | 0.344221   | i371       |
| B2    | -775.781313 | -775.858117 | 0.401843   | 0.426607   | 0.348884   | i976       | -775.781313 | -775.858117 | 0.401843   | 0.426607   | 0.348884   | i976       |

|       | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} | TS_{22-23} | TS_{33-31} |
|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| R1    | -775.730544 | -775.804339 | 0.394914   | 0.421093   | 0.340559   | i597       | -774.520358 | -774.593636 | 0.374874   | 0.399720   | 0.321949   | i545       |
| R3    | -775.730544 | -775.804339 | 0.394914   | 0.421093   | 0.340559   | i597       | -775.518760 | -775.592790 | 0.374091   | 0.398268   | 0.321586   | i50        |
| I2    | -775.723130 | -775.597439 | 0.375224   | 0.399935   | 0.323057   | i568       | -775.517773 | -775.592210 | 0.373833   | 0.398355   | 0.321707   | i568       |
8. Comparison of the computed gas-phase structure and the X-ray structure of 9b

Table S4. Selected bond distances (Å) and angles (°) of structure 9b (X-ray) / C2 (DFT). M06/def2-TZVP (ultrafine grid) was used for geometry optimization. The DFT computed geometry is in close agreement with the X-ray derived structure. Hydrogen atoms are removed for clarity.

| Geometry structure | X-ray | DFT |
|--------------------|-------|-----|
| Bond               |       |     |
| Ru-C1              | 1.88  | 1.89|
| Ru-Cl              | 2.41  | 2.42|
| Ru-O1              | 2.23  | 2.31|
| C1-C2              | 1.52  | 1.51|
| C2-C3              | 1.52  | 1.53|
| C3-O1              | 1.46  | 1.44|
| C1-C4              | 1.52  | 1.51|
| C4-O2              | 1.43  | 1.41|
| Angle              |       |     |
| Ru-C1-C2           | 115.6 | 115.8|
| C1-C2-C3           | 112.3 | 112.8|
| C2-C3-O1           | 102.9 | 103.6|
| Ru-C1-C4           | 128.6 | 128.2|
| C1-C4-O2           | 110.9 | 111.6|
9. Coordinates

All graphics included in this section were generated using the CYLview program.\(^6\)

**XYZ coordinates (Å) for the molecules present in the hydrogenation of 2-butyne using the neutral catalyst**

![Diagram](image)

\begin{verbatim}
Ru  0.777064  1.278906  1.443995
Cl -0.101411  1.196073 -0.865948
C  0.115427  3.449149  1.463179
C  1.410460  3.331773  0.827023
C  2.330327  2.843646  1.773277
C  1.614112  2.613590  3.000993
C  0.262396  3.050870  2.805823
C -1.100957  4.002884  0.818649
H -1.985267  3.861381  1.441064
H -1.283123  3.514697 -0.141720
H -0.989063  5.076549  0.637005
C  1.762533  3.782686 -0.541526
H  0.889505  3.832377 -1.189202
H  2.474399  3.101756 -1.012137
H  2.223394  4.775831 -0.497542
C  3.796543  2.723912  1.555866
H  4.298468  2.240048  2.394163
H  4.245709  3.714908  1.437237
H  4.028652  2.156858  0.651136
C  2.241044  2.291830  4.310985
H  1.504073  1.959869  5.042880
H  2.735671  3.175907  4.726656
H  2.996958  1.508592  4.228055
C -0.777305  3.142053  3.861300
C -1.780066  2.994767  3.456801
H -0.755321  4.132021  4.327303
H -0.624408  2.408118  4.654282
H -0.175543 -2.442896  1.704246
C -0.231566 -1.670469  0.930064
C  1.121223 -1.539123  0.202746
H -0.984693 -2.014155  0.218565
C -0.718548 -0.384041  1.550267
C  1.959354 -0.418830  0.728752
H  1.666388 -2.485873  0.259763
H  0.926662 -1.347680 -0.854283
C  2.224946 -0.225392  2.090015
H  2.668552 -0.007606  0.012920
C  1.753057 -1.166131  3.180204
\end{verbatim}
### S16

#### A1

![Image of molecular structure]

| Atom | X    | Y    | Z    |
|------|------|------|------|
| Ru   | 0.494118 | 1.639484 | 1.367353 |
| Cl   | -1.754135 | 1.266784 | 0.494887 |
| C    | 1.064388  | 0.625319  | -0.609384 |
| C    | 1.656229  | 0.016799  | 0.283809 |
| H    | -0.298007 | 0.609256  | 2.557482 |
| H    | 0.318652  | 0.110212  | 2.263078 |
| C    | 2.486557  | -0.991405 | 0.938778 |
| C    | 0.527529  | 1.048533  | -1.894662 |
| C    | 0.417360  | 3.813813  | 1.062701 |
| C    | 1.741726  | 3.373919  | 0.796008 |
| C    | 2.272463  | 2.768550  | 1.983353 |
| C    | 1.266644  | 2.851710  | 2.989025 |
| C    | 0.105837  | 3.482995  | 2.427391 |
| C    | -0.503026 | 4.512896  | 0.132520 |
| H    | -1.491144 | 4.047762  | 0.147460 |
| H    | -0.140087 | 4.047759  | -0.895766 |
| H    | -0.614041 | 5.564099  | 0.416170 |
| C    | 2.522908  | 3.571877  | -0.451454 |
| C    | 1.902631  | 3.940839  | -1.268155 |
| H    | 3.000170  | 2.645262  | -0.779707 |
| H    | 3.318253  | 4.304606  | -0.283445 |
| C    | 3.670247  | 2.293297  | 2.148382 |
| H    | 3.761553  | 1.590941  | 2.978995 |
| H    | 4.351218  | 3.127725  | 2.348530 |
| H    | 4.029901  | 1.792029  | 1.246969 |
| C    | 1.411650  | 2.391595  | 4.395203 |
| C    | 1.411650  | 2.391595  | 4.395203 |
| H    | 0.448443  | 2.117643  | 4.828008 |
| H    | 1.842606  | 3.180014  | 5.019699 |
| H    | 2.065261  | 1.520029  | 4.463301 |
| C    | -1.156131 | 3.846214  | 3.122561 |
| H    | -2.020917 | 3.625612  | 2.493919 |
| H    | -1.180147 | 4.912492  | 3.370889 |
| H    | -1.276385 | 3.286452  | 4.051224 |
| H    | -0.563409 | 1.057187  | -1.851111 |
| H    | 0.850139  | 0.370063  | -2.688683 |
| H    | 0.850404  | 2.058120  | -2.152414 |
| H    | 3.184971  | -0.539980 | 1.647458 |
| H    | 3.063577  | -1.559354 | 0.204181 |
| H    | 1.867518  | -1.695875 | 1.500799 |
| Element | x    | y    | z    |
|---------|------|------|------|
| Ru      | -0.218908 | 0.164546 | -0.484334 |
| Cl      | -0.890211  | -2.073672 | -1.152513  |
| C       | -2.239399  | 0.024219  | 0.526188   |
| C       | -2.374164  | 0.847416  | -0.380502  |
| H       | -0.381352  | 0.308265  | -2.073003  |
| H       | -0.447370  | 1.473428  | -1.343999  |
| C       | -3.023368  | 1.793243  | -1.282807  |
| C       | -2.531285  | -0.951332 | 1.568103   |
| C       | 1.242468   | -0.735314 | 1.047389   |
| C       | 0.790025   | 0.477511  | 1.603432   |
| C       | 1.058589   | 1.525732  | 0.672595   |
| C       | 1.789154   | 0.955132  | -0.432336  |
| C       | 1.870303   | -0.448623 | -0.224645  |
| C       | 1.157496   | -2.091901 | 1.642399   |
| H       | 0.615614   | -2.767868 | 0.973060   |
| H       | 0.643877   | -2.083402 | 2.604373   |
| H       | 2.157242   | -2.507580 | 1.797930   |
| C       | 0.171331   | 0.702930  | 2.933810   |
| H       | -0.033586  | -0.230327 | 3.457757   |
| H       | -0.763737  | 1.263810  | 2.854476   |
| H       | 0.844178   | 1.293648  | 3.563361   |
| C       | 0.803091   | 2.967950  | 0.931512   |
| H       | 0.876771   | 3.557393  | 0.016916   |
| H       | 1.520811   | 3.377089  | 1.650735   |
| H       | -0.197794  | 3.121862  | 1.341924   |
| C       | 2.422924   | 1.712041  | -1.544714  |
| H       | 2.445329   | 1.123541  | -2.462413  |
| H       | 3.453500   | 1.978458  | -1.291480  |
| H       | 1.884554   | 2.635773  | -1.760652  |
| C       | 2.581384   | -1.449454 | -1.058221  |
| H       | 1.973209   | -2.347132 | -1.186322  |
| H       | 3.529444   | -1.741426 | -0.594264  |
| H       | 2.800696   | -1.055860 | -2.051080  |
| H       | -1.975847  | -0.756240 | 2.487261   |
| H       | -2.265184  | -1.949009 | 1.210116   |
| H       | -3.597547  | -0.938681 | 1.807950   |
| H       | -2.565870  | 2.783496  | -1.215059  |
| H       | -4.085464  | 1.887223  | -1.044835  |
| H       | -2.928434  | 1.460308  | -2.318371  |
TS_{A2-A3}

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Ru   | -0.227446 | 0.416746 | 0.084648 |
| Cl   | -1.284378 | 0.835405 | -2.061778 |
| C    | -2.036053 | -0.712172 | 0.365763 |
| C    | -2.230171 | 0.318295  | 1.059339 |
| H    | -0.319826 | 2.008039 | 0.024221 |
| H    | -0.907287 | 1.027833 | 1.424623 |
| C    | -3.156748 | 1.254846 | 1.712698 |
| C    | -2.498059 | -1.913999 | -0.324392 |
| C    | 1.393036  | -0.868488 | -0.890442 |
| C    | 1.076858  | -1.499364 | 0.334834 |
| C    | 1.269641  | -0.553866 | 1.387057 |
| C    | 1.787456  | 0.655309  | 0.807597 |
| C    | 1.825087  | 0.475925 | -0.612421 |
| C    | 1.305834  | -1.457700 | -2.249892 |
| H    | 0.682252  | -0.838231 | -2.899761 |
| H    | 0.879539  | -2.460903 | -2.233560 |
| H    | 2.302576  | -1.523108 | -2.698480 |
| C    | 0.673247  | -2.912758 | 0.540823 |
| H    | 0.257298  | -3.357459 | -0.362361 |
| H    | -0.067009 | -3.008191 | 1.338057 |
| H    | 1.540073  | -3.513216 | 0.835340 |
| C    | 1.105147  | -0.846939 | 2.834926 |
| H    | 1.098866  | 0.064670  | 3.429260 |
| H    | 1.918206  | -1.481303 | 3.207186 |
| H    | 0.166869  | -1.375687 | 3.027268 |
| C    | 2.292299  | 1.834937  | 1.560116 |
| H    | 2.224975  | 2.744196  | 0.962535 |
| H    | 3.340145  | 1.695749  | 1.847739 |
| C    | 1.719567  | 2.002795  | 2.473253 |
| C    | 2.348491  | 1.417049  | -1.635817 |
| H    | 1.690570  | 1.444349  | -2.506546 |
| H    | 3.346453  | 1.118472  | -1.972506 |
| H    | 2.415292  | 2.432423  | -1.244153 |
| H    | -1.995893 | -2.813073 | 0.039774 |
| H    | -2.284736 | -1.814641 | -1.392411 |
| H    | -3.574169 | -2.056029 | -0.194601 |
| H    | -2.843431 | 1.509399  | 2.727857 |
| H    | -4.159529 | 0.826759  | 1.755283 |
| H    | -3.199750 | 2.184018  | 1.138115 |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Ru   | -0.097135 | -0.130895 | -0.467618 |
| Cl   | -0.923584 | -2.377924 | -0.786020 |
| C    | -1.952942 | 0.156911  | 0.310164  |
| C    | -2.256253 | 1.009526  | -0.656671 |
| H    | 0.319012  | -0.483146 | -1.987120 |
| H    | -1.400027 | 1.501699  | -1.177679 |
| C    | -3.587652 | 1.273236  | -1.282277 |
| C    | -2.778536 | -0.564421 | 1.287855  |
| C    | 1.085908  | -0.473302 | 1.284207  |
| C    | 0.688511  | 0.900018  | 1.373233  |
| C    | 1.194956  | 1.587986  | 0.240010  |
| C    | 1.956245  | 0.664620  | -0.541881 |
| C    | 1.897378  | -0.616032 | 0.095072  |
| C    | 0.832542  | -1.550899 | 2.273121  |
| H    | 0.585132  | -2.485797 | 1.767589  |
| H    | -0.003182 | -1.304103 | 2.929452  |
| H    | 1.713990  | -1.723272 | 2.899033  |
| C    | -0.070152 | 1.541201  | 2.478173  |
| H    | -0.543665 | 0.803472  | 3.125800  |
| H    | -0.849708 | 2.206417  | 2.101371  |
| H    | 0.602373  | 2.141787  | 3.098362  |
| C    | 1.006303  | 3.034324  | -0.036527 |
| H    | 1.149829  | 3.262568  | -1.093509 |
| H    | 1.719186  | 3.640358  | 0.532166  |
| H    | 0.004317  | 3.365352  | 0.245776  |
| C    | 2.749859  | 1.017838  | -1.748563 |
| H    | 2.952230  | 0.140551  | -2.362186 |
| H    | 3.709689  | 1.459316  | -1.462507 |
| H    | 2.225321  | 1.740550  | -2.374968 |
| C    | 2.601508  | -1.859878 | -0.305619 |
| H    | 1.942811  | -2.724313 | -0.208587 |
| H    | 3.484983  | -2.027267 | 0.318731  |
| H    | 2.924539  | -1.815075 | -1.346028 |
| H    | -2.526110 | -0.241708 | 2.503662  |
| H    | -2.587153 | -1.637447 | 1.220835  |
| H    | -3.848215 | -0.379337 | 1.145078  |
| H    | -3.801070 | 2.343339  | -1.340718 |
| H    | -4.387600 | 0.793164  | -0.717084 |
| H    | -3.617861 | 0.880185  | -2.301706 |
TS_{E1-E2}

Ru  -0.368492  -0.179788  0.236650
Cl  -0.218294  -2.316653  1.337415
C   -2.224419  -0.461999  0.287287
C   -2.182324  0.837737  -0.249789
H   -1.142669  -1.101071  -0.901549
H   -2.436220  1.639294  0.450533
C   -2.601548  1.118515  -1.669623
C   -3.264113  -1.447422  0.584243
C   1.936998  -0.212591  0.207085
C   1.439640  0.494335  1.368808
C   0.730456  1.629889  0.914995
C   0.743053  1.601228  -0.523338
C   1.513099  0.475706  -0.942413
C   2.803511  -1.413793  0.263934
H   2.992356  -1.821718  -0.729158
H   2.343734  -2.199151  0.868706
H   3.769286  -1.162073  0.712990
C   1.738416  0.112352  2.770604
H   1.539455  -0.949251  2.932431
H   1.131770  0.676592  3.479350
H   2.791365  0.299879  3.004310
C   0.117153  2.696408  1.744240
H   -0.858186  2.999141  1.354672
H   0.747769  3.591121  1.762436
H   -0.025948  2.367802  2.773828
C   0.291898  2.700223  -1.412603
H   -0.044740  2.330174  -2.382042
H   1.121840  3.390361  -1.584066
H   -0.520301  3.277959  -0.969997
C   1.793696  0.119383  -2.357060
H   2.014519  -0.942368  -2.466259
H   2.650005  0.682369  -2.741705
H   0.938104  0.344574  -2.996714
H   -2.848702  -2.413483  0.865019
H   -3.945668  -1.557640  -0.267365
H   -3.863309  -1.066940  1.418237
H   -2.194822  0.378222  -2.361663
H   -2.286891  2.105968  -2.010198
H   -3.694987  1.088488  -1.753862
TS\textsubscript{E1-C1}

Ru $\quad -0.355473 \quad -0.434415 \quad -0.204525$
Cl $\quad 0.483829 \quad -2.375233 \quad -1.344897$
C $\quad 1.292720 \quad 0.402862 \quad -0.321471$
C $\quad 1.211260 \quad 0.320847 \quad 1.070044$
H $\quad -0.244611 \quad -1.427773 \quad 1.038652$
H $\quad 0.483829 \quad -2.375233 \quad -1.344897$
C $\quad 2.160299 \quad -0.575491 \quad 1.823289$
C $\quad 2.250077 \quad 0.727857 \quad -1.344897$
C $\quad 1.837865 \quad 0.043012 \quad -1.903427$
C $\quad 1.501394 \quad 1.257712 \quad -1.283796$
H $\quad -0.244611 \quad -1.427773 \quad 1.038652$
H $\quad 0.878007 \quad 1.200341 \quad 1.627032$
H $\quad 0.244611 \quad -1.427773 \quad 1.038652$
H $\quad -0.483829 \quad -2.375233 \quad -1.344897$
H $\quad -0.244611 \quad -1.427773 \quad 1.038652$
H $\quad 0.483829 \quad -2.375233 \quad -1.344897$
H $\quad 0.244611 \quad -1.427773 \quad 1.038652$
H $\quad 0.878007 \quad 1.200341 \quad 1.627032$
H $\quad 0.244611 \quad -1.427773 \quad 1.038652$
H $\quad 0.483829 \quad -2.375233 \quad -1.344897$
H $\quad 0.878007 \quad 1.200341 \quad 1.627032$
H $\quad 0.244611 \quad -1.427773 \quad 1.038652$
Ru  -0.382869  -0.329275  0.084149
Cl  -0.196930  -2.640475  0.656716
C   1.301582   0.144078  -0.568348
C   1.528292   0.330149   0.798890
H   0.343111  -0.257806  1.660914
H   1.536105   1.364730  1.162362
C   2.377915  -0.602255  1.619264
C   1.989332   0.500498  -1.810337
C  -1.671560   0.074874   1.841165
C  -1.396282  1.269229  -1.102933
C  -2.000403  1.152903   0.193415
C  -2.628421  -0.129334  0.254810
C  -2.412408  -0.782801  -0.996116
C  -1.315041  -0.205234  -3.258605
H  -0.869097  -1.143542  -3.373267
H  -0.402157   0.524767  -3.648545
H  -2.190644  -0.167903  -3.902743
C  -0.758782   2.511435   1.616530
H  -0.133751   2.323181  -2.490086
H  -0.132230   2.838321  -0.855396
H  -1.519941   3.241252  -1.909767
C  -2.072628   2.238331   1.206712
H  -2.277861   1.840032   2.200777
H  -2.864300   2.954000   0.961779
H  -1.133999   2.793086   1.264544
C  -3.415596  -0.702709   1.378644
H  -3.121620  -1.736785   1.571991
H  -4.487086  -0.697166   1.153466
H  -3.265240  -0.141028   2.501213
C  -2.926173  -2.130041  -1.341400
H  -2.605834  -2.440901  -2.335815
H  -4.019998  -2.137701  -1.318491
H  -2.568019  -2.876156  -0.627096
H  1.428104   0.251994  -2.711799
H  2.941442  -0.041324  -1.842807
H  2.248166   1.566750  -1.821460
H  2.337189  -1.618658  1.228303
H  2.042007  -0.637238   2.657214
H  3.419724  -0.263537   1.615888
TSCl_C2

C  -1.666469  0.508786  -0.392428
C  -1.272165  0.802026   0.936024
C  -1.100563 -0.442252  1.643097
C  -1.495034 -1.501462  0.756397
C  -1.804462 -0.917322  -0.487909
Ru  0.398810 -0.400435  0.055485
C   2.387028 -0.189478  0.866459
C   3.597746 -0.716113  0.139432
C  -1.173339  2.150866  1.551564
C  -0.775026 -0.586135  3.086757
C  -1.552351 -2.951391  1.085199
C  -2.255557 -1.627515  -1.709058
C  -1.984552  1.465781  -1.483816
Cl   1.037297 -1.387875  -2.025576
C   1.668815  0.914216  0.359671
C   1.896665  2.358419  0.293145
H   1.320763 -1.578364  0.626345
H   2.454810 -0.288088  1.955027
H  -0.950101  2.923230  0.814331
H  -0.402391  2.192310  2.322983
H  -2.122478  2.419430  2.025362
H  -0.139341  0.230661  3.434829
H  -0.241508 -1.518709  3.280009
H  -1.678307 -0.586982  3.705583
H  -1.215142 -3.561363  0.245202
H  -2.570878 -3.264026  1.336480
H  -0.914686 -3.191577  1.937066
H  -1.720356 -1.275176  -2.592026
H  -3.325477 -1.456373  -1.866202
H  -2.089408 -2.702005  -1.635780
H  -3.065548  1.577064  -1.621898
H  -1.565611  1.125621  -2.433323
H  -1.574930  2.456919  -1.281115
H   1.076409  2.900535  -0.180376
H   2.803119  2.531674  -0.299540
H   2.091943  2.786548  1.283731
H   3.469801 -0.637262  -0.940070
H   3.786863 -1.764916  0.374600
H   4.480505 -0.139589  0.435023
Z2

Ru  -0.335768 -0.264955  -0.276593
Cl  -0.184754 -2.655262  -0.017896
C   -2.173235 -0.555370  -0.353907
C   -2.138566  0.832765  -0.556107
H   -0.488821 -0.569774  -1.831087
C   -2.745085  1.735232   0.485076
H   -2.243172  1.204599  -1.578327
C   -3.201486 -1.592808  -0.352816
C   1.700986 -0.284898  -0.181973
C   1.443355 -0.052847   1.146180
C   0.746652  1.170645   1.129293
C   0.792258  1.680336  -0.219295
C   1.598605  0.799448  -0.997620
C   2.849736 -1.432029  -0.549893
H   2.994879 -1.483620  -1.628631
H   2.422116 -2.367724  -0.215615
H   3.833382 -1.305449  -0.083482
C   1.700562 -0.932181   2.312604
H   1.411114 -1.962845   2.090302
H   1.144661 -0.605998   3.192017
H   2.764778 -0.930758   2.568648
C   0.162872  1.858043   2.311504
H   -0.597921  2.584625   2.029147
H   0.941009  2.396515   2.861971
H   -0.297000  1.150085   3.003036
C   0.330270  3.013073  -0.685875
H   -0.132805  2.954578  -1.672852
H   1.177168  3.702757  -0.762402
H   -0.393403  3.459359  -0.004850
C   1.971352  1.022951  -2.418353
H   2.206891  0.086732  -2.924451
H   2.849231  1.673072  -2.489290
H   1.162010  1.503053  -2.970483
H   -2.821308 -2.562938  -0.039310
H   -3.656228 -1.632972  -1.354938
H   -4.017179 -1.276260   0.308133
H   -2.361804  2.756721   0.434043
H   -2.573643  1.352969   1.493798
H   -3.829822  1.798674   0.337397
| Atoms | X     | Y     | Z     |
|-------|-------|-------|-------|
| Ru    | -0.354161 | -0.097101 | -0.187275 |
| Cl    | -1.090814  | -2.366754  |  0.179861  |
| C     | -2.165968  |  0.273203  | -0.496857  |
| C     | -1.654196  |  1.578658  |  0.479427  |
| H     | -0.906028  |  0.321277  |  1.700941  |
| C     | -2.089321  |  2.528500  |  0.602259  |
| H     | -1.422926  |  2.059572  | -1.432329  |
| C     | -3.482832  | -0.346264  | -0.629957  |
| C     |  1.784365  | -0.921156  | -0.091516  |
| C     |  1.370386  | -0.485868  |  1.224507  |
| C     |  1.134682  |  0.902440  |  1.70002   |
| C     |  1.357857  |  1.322231  | -0.189228  |
| C     |  1.799269  |  0.203285  |  0.939941  |
| C     |  2.204894  | -2.302854  | -0.425269  |
| H     |  2.344508  | -2.433611  | -1.498600  |
| H     |  1.457139  | -3.027056  | -0.094576  |
| H     |  3.152166  | -2.541941  |  0.068358  |
| C     |  1.310380  | -1.363110  |  2.418703  |
| H     |  0.706616  | -2.251278  |  2.216727  |
| H     |  0.875066  | -0.846499  |  3.274529  |
| H     |  2.314517  | -1.694676  |  2.701649  |
| C     |  0.800755  |  1.773845  |  2.326688  |
| H     |  0.346406  |  2.712926  |  2.012844  |
| H     |  1.703633  |  2.019994  |  2.894629  |
| H     |  0.105715  |  1.283569  |  3.010441  |
| C     |  1.363833  |  2.731739  | -0.684389  |
| H     |  1.021349  |  2.791540  | -1.719261  |
| H     |  2.376594  |  3.146360  | -0.651605  |
| H     |  0.724414  |  3.381650  | -0.084676  |
| C     |  2.192070  |  0.231068  | -2.372401  |
| H     |  2.051337  | -0.741365  | -2.845415  |
| H     |  3.245448  |  0.507548  | -2.480999  |
| H     |  1.601774  |  0.958058  | -2.932232  |
| H     |  3.459290  | -1.418861  | -0.447372  |
| H     |  3.903259  | -0.146428  | -1.621651  |
| H     | -4.154098  |  0.132876  |  0.092686  |
| H     | -1.378069  |  3.346180  |  0.743500  |
| H     | -2.209573  |  2.015514  |  1.559102  |
| H     | -3.050596  |  2.988801  |  0.345231  |
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| Ru      | 1.136561| 0.413449| -1.828358|
| Cl      | 3.358924| -0.240329| -2.553361|
| C       | 2.162369| 0.962564| -0.166814|
| C       | 1.929376| -0.226005| 0.353130|
| H       | 0.879059| -1.086299| -2.337665|
| H       | 1.702569| -1.045474| -0.380363|
| C       | 1.837040| -0.647250| 1.783327|
| C       | 2.767560| 2.187134| 0.367004|
| C       | 0.854646| 2.297732| -2.832018|
| C       | -0.134008| 2.208962| -1.801129|
| C       | -0.970439| 1.080960| -2.099024|
| C       | -0.547797| 0.516108| -3.324106|
| C       | 0.606541| 1.224802| -3.766501|
| C       | 1.918450| 3.322742| -2.995214|
| H       | 2.883875| 2.848048| -3.185873|
| H       | 2.024767| 3.937115| -2.100214|
| H       | 1.699789| 3.988789| -3.235576|
| C       | -0.388487| 3.163811| -0.689285|
| H       | 0.374453| 3.940565| -0.640006|
| H       | -0.417541| 2.660618| 0.280440|
| H       | -1.352794| 3.662061| -0.827605|
| C       | -2.147155| 0.662569| -1.285604|
| H       | -2.357669| -0.400512| -1.409709|
| H       | -3.044829| 1.215644| -1.582481|
| H       | -1.984795| 0.847325| -0.222331|
| C       | -1.221415| -0.590668| -4.051922|
| H       | -0.518545| -1.149604| -4.669402|
| H       | -1.998681| -0.189674| -4.710039|
| H       | -1.696731| -1.294189| -3.367668|
| C       | 1.346759| 0.994944| -5.031202|
| H       | 2.388851| 1.297796| -4.335593|
| H       | 0.893293| 1.562007| -5.850908|
| H       | 1.347203| -0.060983| -5.304155|
| H       | 2.106132| 3.053565| 0.300893|
| H       | 3.653177| 2.416510| -0.236004|
| H       | 3.092025| 2.072428| 1.406303|
| H       | 0.817391| -0.942722| 2.045086|
| H       | 2.128105| 0.169839| 2.446091|
| H       | 2.483090| -1.503898| 1.989992|
| Atom | X    | Y    | Z    |
|------|------|------|------|
| Ru   | 0.343643 | 0.062379 | -0.206990 |
| Cl   | -0.395845 | 2.108155 | -1.304511 |
| C    | 0.186483  | -0.910687 | 1.857398  |
| H    | -1.194427 | 0.349245  | -2.932196 |
| H    | -0.904547 | -1.246893 | 3.670537  |
| C    | 0.656552  | 0.200728  | -4.000697 |
| C    | 0.553161  | -2.343594 | 1.993482  |
| C    | 0.070934  | -1.318490 | 1.488534  |
| C    | -1.261069 | -1.035644 | 1.058893  |
| C    | -1.474027 | 0.348515  | 1.211971  |
| C    | -0.301685 | 0.937518  | 1.822370  |
| C    | 0.639182  | -0.088543 | 2.009308  |
| C    | 0.649652  | -2.676549 | 1.668668  |
| H    | 1.739931  | -2.656569 | 1.641361  |
| H    | 0.312086  | -3.367450 | 0.894332  |
| H    | 0.350360  | -3.098246 | 2.633826  |
| C    | -2.236655 | -2.030164 | 0.540343  |
| H    | -1.733568 | -2.883477 | 0.081826  |
| H    | -2.896324 | -1.591846 | -0.210425 |
| H    | -2.865789 | -2.420424 | 1.346438  |
| C    | -2.715388 | 1.096311  | 0.903223  |
| H    | -2.496494 | 1.973161  | 0.288990  |
| H    | 3.186754  | 1.440874  | 1.828957  |
| H    | 3.437853  | 0.480170  | 0.367468  |
| C    | -0.189083 | 2.367720  | 2.202431  |
| H    | 0.818308  | 2.613425  | 2.539128  |
| H    | -0.882081 | 2.614307  | 3.013042  |
| H    | -0.423717 | 3.011947  | 1.539090  |
| C    | 1.960206  | 0.020306  | 2.682823  |
| H    | 2.691542  | -0.659087 | 2.243285  |
| H    | 1.874968  | -0.227714 | 3.745480  |
| H    | 2.364705  | 1.029799  | 2.606364  |
| H    | 1.184079  | -2.723209 | -1.192186 |
| H    | 1.038513  | -2.530786 | -2.959382 |
| H    | -0.373859 | -2.934295 | -2.017891 |
| H    | 1.080153  | 1.075694  | -3.507209 |
| H    | 0.240194  | 0.511364  | -4.959851 |
| H    | 1.460643  | -0.512732 | -4.198001 |
| H    | 1.680923  | -0.773907 | -0.228289 |
| H    | 1.730492  | 0.796349  | -0.521874 |
R2

Ru  0.246622  0.007445  -0.462823
C  1.922009  0.664501  0.227671
C  3.145489 -0.124064  0.560587
H  2.880069 -1.082013  1.007395
H  3.773434  0.435880  1.265350
C  3.942030 -0.716975  0.484909
H  2.149768  2.113487  0.884909
H  3.101651  2.430517  0.038956
H  4.163693  0.537833  1.252102
C  1.862953  1.466741  -0.122764
C  1.256865  0.855335  1.084795
C  -1.515312 -0.524125  0.929948
C  -1.921779 -0.770163  -0.437759
H  -2.187562 -0.188249  -3.139923
H  -1.621171  1.469701  -2.993192
H  -3.290519  1.075055  -2.585457
C  -1.408712  2.929750  -0.460958
H  -0.737180  3.468471  0.209261
H  -2.411997  3.342482  -0.312099
H  -1.109098  3.155184  -1.485162
C  -0.903924  1.557015  2.346397
H  -0.362989  0.903297  3.031971
H  -1.802977  1.907818  2.862800
H  -0.277718  2.431117  2.159061
C  -1.495886 -1.560822  1.989901
H  -0.878693 -2.411161  1.687667
H  -2.509309 -1.928943  2.177379
H  -1.100933 -1.172750  2.929012
C  -2.359803 -2.089926  -0.954462
H  -3.305640 -2.394498  -0.495405
H  -1.613998 -2.857407  -0.732305
H  -2.505195 -2.068210  -2.034705
Cl  1.020342 -2.274908  -0.142242
H  0.759789  0.384951  -1.924648
H  0.618132  1.166781  -1.472991
TSR2-R3

Ru    0.090255  0.195514  -0.262610
C   1.072225  1.814438  0.189512
C   2.557211  1.972549  0.152032
H   3.030514  1.106116  0.618053
H   2.848209  2.874659  0.705029
C   3.056032  2.085232  -1.285948
C   0.402775  3.099481  0.529324
H   0.623565  3.318478  1.581822
H   -0.676413  3.097231  0.391234
H    0.836932  3.929734  -0.043587
H    2.538246  2.881923  -1.828492
H    2.890400  1.147165  -1.816067
H    4.123534  2.308523  -1.298924
C   -1.851842  -0.503015  -1.047091
C   -2.107400  0.594578  -0.148228
C   -1.751355  0.177268  1.164814
C   -1.233101  -1.140270  1.073386
C   -1.313494  -1.576399  -0.291069
C   -2.223491  -0.523752  -2.487059
H   -1.625170  -1.245595  -3.043552
H   -2.074817  0.452098  -2.951610
H   -3.277332  -0.792995  -2.612276
C   -2.852115  1.828568  -0.519386
H   -2.780776  2.598566  0.249952
H   -3.915880  1.606640  -0.653540
H   -2.488905  2.256441  -1.455587
C   -1.914944  0.965342  2.415076
H   -1.109560  0.762898  3.122756
H   -2.859262  0.721947  2.912343
H   -1.919725  2.038999  2.220217
C   -0.753885  -1.985876  2.194175
H   0.257055  -2.353107  1.997683
H   -1.409600  -2.852630  2.321328
H   -0.735242  -1.437747  3.136259
C   -0.934953  -2.931566  -0.766653
H   -1.649678  -3.686147  -0.422820
H   0.053806  -3.209018  -0.393501
H   -0.900230  -2.976164  -1.855738
Cl   2.000399  -1.139696  0.394596
H   0.754893  -0.248405  -1.633378
H   0.217939  1.399705  -1.325465
R3

Ru  0.133337  -0.108771  -0.504750
C  1.907593  0.643042  0.161411
C  3.150043  -0.125757  0.544532
H  2.887305  -1.131152  0.878494
H  3.627460  0.392102  1.384884
C  4.134386  -0.237663  -0.108771
C  1.999743  2.075406  0.608778
H  1.950794  2.128243  1.700979
H  1.220872  2.713160  0.192056
H  2.970916  2.505232  0.327728
H  4.397533  0.746828  -1.008898
H  3.696463  -0.829883  -1.415850
H  5.057789  -0.727997  -0.296035
C  -1.904725  0.475785  -1.139646
C  -1.462675  1.495172  -0.236048
C  -1.210841  0.885752  1.018444
C  -1.459033  -0.519999  0.890886
C  -1.933744  -0.770345  -0.442887
C  -2.374714  0.738216  -2.525300
H  -2.391663  -0.172518  -3.123488
H  -1.729224  1.455388  -0.304738
H  -3.387292  1.154631  -2.514803
C  -1.411456  2.943004  -0.566390
H  -0.918827  3.524360  0.213302
H  -2.421870  3.346745  -0.687915
H  -0.878728  3.120279  -1.503385
C  -0.838138  1.561473  2.287362
C  -0.120407  0.970804  2.859279
H  -1.724501  1.694522  2.915574
H  -0.403527  2.546873  2.120860
C  -1.378990  -1.526594  1.978198
H  -1.136888  -2.512018  1.581005
H  -2.334455  -1.595635  2.509113
H  -0.607155  -1.269560  2.705155
C  -2.401454  -2.085713  -0.950081
H  -3.354224  -2.368161  -0.491910
H  -1.670364  -2.867220  -0.732460
H  -2.540799  -2.065146  -2.031510
Cl  1.125461  -2.302657  -0.451899
H  0.004057  -0.657638  -1.390937
H  1.771545  0.627509  -1.017262
| Atomo | x       | y       | z       |
|-------|---------|---------|---------|
| Ru    | 0.001457| 0.000140| -1.029809|
| C     | 1.980102| 0.389243| -0.354689|
| C     | 2.581372| -0.195908| 0.893664|
| H     | 2.327705| -1.260812| 0.929591|
| H     | 2.142114| 0.273746| 1.782069|
| C     | 4.093380| -0.038456| 0.952878|
| C     | 2.093641| 1.887039| -0.509332|
| H     | 1.804000| 2.424924| 0.398161|
| H     | 1.478370| 2.265337| -1.339139|
| H     | 1.321327| 2.185671| -0.755315|
| H     | 4.387680| 1.014097| 0.977901|
| H     | 4.560909| -0.493755| 0.075965|
| H     | 4.510904| -0.517406| 1.840987|
| C     | -2.123283| 0.593342| -1.023201|
| C     | -1.470537| 1.524164| -0.158023|
| C     | -0.882829| 0.810282| 0.913273|
| C     | -1.105608| -0.586846| 0.689628|
| C     | -1.921173| -0.722841| -0.500729|
| C     | -2.969114| 0.977523| -2.184385|
| H     | -3.141815| 0.133136| -2.851189|
| H     | -2.504214| 1.770171| -2.772634|
| H     | -3.942962| 1.345934| -1.845811|
| C     | -1.496000| 2.998642| -0.324841|
| C     | -0.725262| 3.488352| 0.270674|
| H     | -2.464639| 3.405080| -0.015032|
| H     | -1.347153| 3.283943| -1.368364|
| C     | -0.289808| 1.419837| 2.130373|
| H     | 0.287724| 0.698517| 2.706708|
| H     | -1.098104| 1.792862| -2.779970|
| H     | 0.360355| 2.265817| 1.902996|
| C     | -0.732778| -1.703465| 1.592713|
| H     | -0.518158| -2.607957| 1.023179|
| H     | -1.549467| -1.924267| 2.288220|
| H     | 0.155361| -1.467104| 2.180252|
| C     | -2.504343| -1.995287| -0.993201|
| H     | -3.325652| -2.322780| -0.347768|
| H     | -1.750331| -2.783697| -1.017207|
| H     | -2.890979| -1.887446| -2.007065|
| Cl    | 0.999846| -2.105599| -1.628919|
| H     | -0.547403| -0.358487| -2.481722|
| H     | 2.444963| -0.105598| -1.219679|
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Ru      | 0.031068 | -0.181934 | 0.018920 |
| C       | 2.088958 | 0.376623  | 0.085002  |
| C       | 2.791887 | 0.842942  | 1.329377  |
| H       | 2.990145 | -0.002698 | 1.992050  |
| H       | 2.154581 | 1.541353  | 1.886926  |
| C       | 4.115645 | 1.517475  | 0.998720  |
| C       | 1.488820 | 1.429034  | -0.750302 |
| H       | 1.604433 | 2.437330  | -0.344445 |
| H       | 0.300316 | 1.390696  | -0.825989 |
| H       | 1.747554 | 1.376522  | -1.807002 |
| H       | 3.966417 | 2.401960  | 0.374082  |
| H       | 4.768685 | 0.835919  | 0.448259  |
| H       | 4.643489 | 1.832092  | 1.901577  |
| C       | -1.809676 | 0.054805  | 1.131222  |
| C       | -0.743340 | 0.271025  | 2.064260  |
| C       | -0.015637 | -0.950080 | 2.189682  |
| C       | -0.571148 | -1.894109 | 1.289311  |
| C       | -1.704549 | -1.292616 | 0.645920  |
| C       | -2.899444 | 1.025528  | 0.847132  |
| H       | -3.388847 | 0.811650  | -0.103250 |
| H       | -2.519015 | 2.047242  | 0.798500  |
| H       | -3.661812 | 0.995175  | 1.632539  |
| C       | -0.565032 | 1.509378  | 2.868999  |
| H       | 0.395782  | 1.525033  | 3.383936  |
| H       | -1.348369 | 1.599248  | 3.628602  |
| H       | -0.617846 | 2.402694  | 2.242062  |
| C       | 1.059433  | -1.255378 | 3.166800  |
| H       | 1.863475  | -1.840376 | 2.716901  |
| H       | 0.648090  | -1.849152 | 3.989208  |
| H       | 1.497293  | -0.356725 | 3.599210  |
| C       | -0.128934 | -3.296814 | 1.096035  |
| H       | -0.172389 | -3.575980 | 0.042414  |
| H       | -0.768256 | -3.983228 | 1.660739  |
| H       | 0.899512  | -3.441776 | 1.428158  |
| C       | -2.630069 | -2.008424 | -0.270658 |
| H       | -3.246244 | -2.726902 | 0.279109  |
| H       | -2.074009 | -2.554197 | -1.034967 |
| H       | -3.297272 | -1.315302 | -0.784039 |
| Cl      | 0.804944  | -1.563317 | -1.819878 |
| H       | -0.966940 | 0.126903  | 1.185879  |
| H       | 2.665696  | -0.356300 | 0.476400  |
D2

Ru   0.006558  0.561177  -0.272290
C    2.173059  0.071699  -0.479729
C    2.990011  -0.053067  0.767487
H    2.735316  -0.952796  1.330176
H    2.798980  0.803075  1.421917
C    4.479601  -0.099357  0.420776
C    1.952148  1.319466  -1.046724
H    2.308249  2.202250  -0.525473
H    0.481582  1.791399  0.767487
H    1.795268  1.433540  -2.110442
H    4.798312  0.815863  -0.092250
H    4.698805  -0.936784  -0.246275
H    5.098247  -0.211185  1.313470
C   -1.563121  0.689299  1.189549
C   -0.452406  -0.016622  1.798613
C   -0.352386  -1.300569  1.172249
C   -1.302217  -1.354483  0.143632
C   -2.048315  -0.117263  0.126399
C   -2.163532  1.958282  1.678714
H   -2.631561  2.514118  0.866062
H   -1.415885  2.609912  2.131634
H   -2.930462  1.754009  2.432277
C    0.239891  0.387353  3.050196
H    1.279655  0.058586  3.063695
H   -0.256225  -0.051368  3.922079
H    0.236332  1.470216  3.176910
C    0.544081  -2.417662  1.572094
H    1.137344  -2.788275  0.732640
H   -0.043055  -3.260007  1.949561
H    1.230388  -2.121838  2.365020
C   -1.566312  -2.505373  -0.748187
H   -1.407418  -2.224775  -1.793819
H   -2.606197  -2.828761  -0.644602
H   -0.919850  -3.352254  -0.518028
C   -3.208542  0.149212  -0.760557
H   -4.079206  -0.438720  -0.452087
H   -2.970905  -0.112226  -1.793668
H   -3.490136  1.202247  -0.741737
Cl  -0.197112  -0.131879  -2.590132
H   -0.408171  1.950381  -0.914358
H    2.173166  -0.793499  -1.140004
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Ru      | 0.230361 | -0.182283 | -0.182731 |
| Cl      | 0.865162 | -2.455335 | -0.653060 |
| C       | 2.150668 | 0.522072 | -0.666634 |
| C       | 2.393575 | 0.144126 | 0.749846 |
| H       | 1.478584 | -0.419554 | 1.213846 |
| C       | 2.462226 | 1.027931 | 1.388010 |
| C       | 3.525159 | -0.842261 | 0.984674 |
| C       | 2.334415 | 1.962233 | -1.042962 |
| C       | -1.275842 | 1.281517 | -0.642808 |
| C       | -0.950744 | 1.421360 | 0.733347 |
| C       | -1.347733 | 0.200868 | 1.404034 |
| C       | -1.900001 | -0.681504 | 0.462389 |
| C       | -1.803285 | -0.055847 | -0.827595 |
| C       | -1.202263 | 2.339099 | -1.683578 |
| H       | -1.012112 | 1.913236 | -2.669958 |
| H       | -0.403889 | 3.053025 | -1.476787 |
| H       | -2.142014 | 2.897507 | -1.739746 |
| C       | -0.474636 | 2.649255 | 1.423684 |
| H       | -0.080833 | 3.379835 | 0.716406 |
| H       | 0.315378  | 2.430728 | 2.146602 |
| H       | -1.289710 | 3.131170 | 1.973846 |
| C       | -1.192702 | -0.035485 | 2.864126 |
| H       | -1.166874 | -1.098935 | 3.102369 |
| H       | -2.023855 | 0.413568 | 3.417344 |
| H       | -0.274617 | 0.414761 | 3.247204 |
| C       | -2.425029 | -2.049662 | 0.692474 |
| H       | -1.856175 | -2.781823 | 0.112255 |
| H       | -3.473540 | -2.116819 | 0.388118 |
| H       | -2.361699 | -2.336197 | 1.742111 |
| C       | -2.348898 | -0.640435 | -2.080064 |
| H       | -1.977364 | -0.115908 | -2.960762 |
| H       | -3.442529 | -0.588144 | -2.029494 |
| H       | -2.060134 | -1.688677 | -2.174611 |
| H       | 1.924908  | 2.167942 | -2.034744 |
| H       | 3.396633  | 2.236158 | -1.067920 |
| H       | 1.842739  | 2.630440 | -0.330129 |
| H       | 3.354690  | -1.749373 | 0.402805 |
| H       | 3.612796  | -1.119705 | 2.036530 |
| H       | 4.470322  | -0.396801 | 0.667092 |
| H       | 2.658232  | -0.156026 | -1.354129 |
| H       | 0.455332  | -0.098159 | -1.747234 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Ru      | 0.281824 | -0.462667 | -0.050415 |
| C       | 2.274015  | -0.525684  | 1.017383  |
| C       | 2.175545  | -1.511696  | 2.135455  |
| H       | 1.411497  | -1.221045  | 2.860784  |
| H       | 3.130718  | -1.586230  | 2.668394  |
| H       | 1.937069  | -2.512571  | 1.766573  |
| C       | 1.796624  | 0.766214   | 1.077102  |
| H       | 1.333159  | 1.106842   | 2.001398  |
| C       | 2.319536  | 1.830787   | 0.162409  |
| C       | -1.271390 | 1.007905   | 0.109884  |
| C       | -1.298050 | 0.193441   | 1.281515  |
| C       | -1.499452 | -1.157328  | 0.853484  |
| C       | -1.711297 | -1.157628  | -0.573603 |
| C       | -1.546932 | 0.166451   | -1.035066 |
| C       | -1.157221 | 2.486987   | 0.064704  |
| H       | -0.656612 | 2.821894   | -0.084587 |
| H       | -0.596317 | 2.877128   | 0.915505  |
| H       | -2.148122 | 2.952694   | 0.082249  |
| C       | -1.222664 | 0.651847   | 2.692266  |
| H       | -0.650515 | -0.039751  | 3.314724  |
| H       | -2.223580 | 0.728967   | 3.128630  |
| H       | -0.756663 | 1.634576   | 2.777499  |
| C       | -1.594636 | -2.348599  | 1.732619  |
| H       | -1.169813 | -3.230222  | 1.249162  |
| H       | -2.639255 | -2.573536  | 1.973930  |
| H       | -1.062077 | -2.195733  | 2.672265  |
| C       | -1.985841 | -2.364850  | -1.391898 |
| H       | -1.696442 | -2.219557  | -2.432248 |
| H       | -3.050388 | -2.617532  | -1.363065 |
| H       | -1.425485 | -3.225825  | -1.023769 |
| C       | -1.617832 | 0.636993   | -2.439424 |
| H       | -2.603740 | 1.055790   | -2.666039 |
| H       | -1.423446 | -0.174824  | -3.140168 |
| H       | -0.875107 | 1.414859   | -2.627595 |
| Cl      | 1.421264  | -1.720849  | -1.677394 |
| H       | 3.001289  | -0.761334  | 0.244104  |
| H       | 2.651648  | 1.399840   | -0.785337 |
| H       | 3.181413  | 2.332581   | 0.617422  |
| H       | 1.577367  | 2.600313   | -0.055292 |
### TS$_{R3-B1'}$

|   |   |   |   |
|---|---|---|---|
| Ru | 0.014614 | -0.041514 | -0.564151 |
| C  | 1.987395 | -0.737679 | -0.187491 |
| C  | 2.073730 | -2.230106 | 0.056058  |
| H  | 1.606773 | -2.590874 | 1.008766  |
| H  | 3.112281 | -2.579437 | 0.107732  |
| H  | 1.582172 | -2.790873 | -0.741403 |
| C  | 2.697236 | 0.087730  | 0.875022  |
| H  | 2.354132 | -0.207917 | 1.873178  |
| H  | 2.434172 | 1.147228  | 0.763063  |
| C  | 4.213218 | -0.040489 | 0.815670  |
| C  | -1.859189 | 1.185745  | -0.043933 |
| C  | -0.926947 | 1.178999  | 1.059259  |
| C  | -0.760176 | 1.160006  | 1.490422  |
| C  | -1.480381 | -0.993164 | 0.560574  |
| C  | -2.201429 | -0.140661 | -0.359141 |
| C  | -2.391335 | 2.422805  | -0.672680 |
| H  | -2.798422 | 2.232282  | -1.655556 |
| H  | -1.620069 | 3.188563  | -0.767976 |
| H  | -3.191679 | 2.841531  | -0.054941 |
| C  | -0.365199 | 2.396196  | 1.694997  |
| H  | 0.498773 | 2.159142  | 2.316415  |
| H  | -1.109019 | 2.893509  | 2.326669  |
| H  | -0.040789 | 3.118373  | 0.942761  |
| C  | -0.111801 | -0.627708 | 2.741854  |
| H  | 0.445771 | -1.554564 | 2.597169  |
| H  | -0.873322 | -0.823236 | 3.503723  |
| H  | 0.576330 | 0.113717  | 3.147272  |
| C  | -1.602107 | -2.470889 | 0.618429  |
| H  | -1.722273 | -2.893824 | -0.379935 |
| H  | -2.473502 | -2.760805 | 1.215670  |
| H  | -0.721411 | -2.929823 | 1.070430  |
| C  | -3.104812 | -0.617480 | -1.434483 |
| H  | -4.052789 | -0.979740 | -1.024606 |
| H  | -2.644240 | -1.432916 | -1.995451 |
| H  | -3.326593 | 0.175663  | -2.149055 |
| Cl | 0.344671 | -1.005677 | 2.686825  |
| H  | -0.409862 | 1.088793  | -1.562726 |
| H  | 2.443531 | -0.524773 | -1.165206 |
| H  | 4.587093 | 0.248654  | -0.170079 |
| H  | 4.537628 | -1.066777 | 1.000939  |
| H  | 4.700006 | 0.596869  | 1.557586  |
TSb1\-b2

Ru  0.772848  -0.853743  -1.633334  -1.633334
C   2.167700  -0.298138  -0.122072  0.900233
H   1.780111  -2.169128  0.900233
H   3.210812  -2.194973  0.900233
H   1.639979  -2.351452  0.857088
C   1.697195  0.442023  1.102945
H   0.771373  -0.016571  1.471688
H   1.442385  1.472300  0.831633
C   2.745137  0.449468  2.202763
H   -0.761049  -0.031730  -2.812992
H   -1.094547  -1.113381  -1.931782
C   -1.309854  1.477700  -0.712484
C   -1.688757  -1.454325  0.519281
H   -2.136844  -2.316065  0.912988
H   -2.752779  -1.711518  0.554141
C   -2.513515  -0.620051  1.204213
C   -1.204259  -3.539572  -1.768973
C   -0.683619  -4.077590  -2.561295
C   -2.253183  -3.852465  -1.782500
C   -0.785569  -3.865335  -0.814334
C   -0.567496  -1.939185  -4.477339
C   -0.583334  -3.028999  -4.467308
C   0.410174  -1.625310  -4.852450
C   -1.329337  -1.598062  -5.184571
Cl  2.627985  -1.072118  -3.157103
H   1.413041  0.592531  -1.242588
H   3.107610  0.102947  -0.504380
H   3.671060  0.913178  1.853442
H   2.989245  -0.566802  2.523513
H   2.405479  1.002069  3.080780
TS_{12.04}

C    -1.203446  0.327775  1.411589
C    -1.102122 -1.068680  1.220224
C    -1.550281 -1.361053 -0.122287
C    -1.998628 -0.139721 -0.710060
C    -1.774277  0.896416  0.210787
Ru    0.274150 -0.115723 -0.220501
C    1.393892 -1.893160 -0.456515
H    1.115776  2.487283  1.326918
C    -0.660433 -2.060037  2.232981
C    -1.734845 -2.705210 -0.725397
C    -2.582505 -0.014195 -2.070244
C    -2.115100  2.328799  0.046294
C    -0.889087  1.101712  2.638156
Cl    1.199354  2.105084 -0.053077
C    2.024931 -0.648692 -0.608896
C    3.373384 -0.123047 -0.851059
H    0.774315 -0.047964 -1.780613
H    1.618691 -2.485910  0.431871
H    0.145891 -1.662543  2.852346
H    -0.299310 -2.978965  1.769787
H    -1.486248 -2.321711  2.897397
H    -1.132607 -3.462768 -0.223615
H    -1.455805 -2.709071 -1.781406
H    -2.782409 -3.017082 -0.662042
H    -2.428084  0.982797 -2.482892
H    -3.659867 -0.206360 -2.050767
H    -2.133963 -0.729764 -2.760824
H    -1.241352  2.960083  0.225899
H    -2.892543  2.614420  0.761484
H    -2.485065  2.544143 -0.956016
H    -1.806098  1.443876  3.128909
H    -0.289082  1.982283  2.396897
H    -0.330426  0.502093  3.357528
H    3.317281  0.925559 -1.145049
H    3.851210 -0.692613 -1.656616
C    4.188805 -0.255060  0.432380
H    4.212727 -1.289253  0.783974
H    3.749178  0.365484  1.214812
H    5.216418  0.070241  0.266348
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -1.479248 | -1.514872 | 0.953550 |
| C    | -0.773376  | -2.568405  | 0.329679  |
| C    | -0.776081  | -2.313676  | -1.091188 |
| C    | -1.569290  | -1.152918  | -1.332487 |
| C    | -1.973540  | -0.640634  | -0.088330 |
| Ru   | 0.355028   | -0.675944  | -0.086302 |
| C    | 2.132166   | -1.673590  | -0.599391 |
| H    | 2.560498   | -1.531401  | -1.592290 |
| C    | -0.181593  | -3.763363  | 0.981242  |
| C    | -0.262473  | -3.225720  | -2.145440 |
| C    | -1.894789  | -0.604418  | -2.674494 |
| C    | -2.839628  | 0.537013   | 0.152794  |
| C    | -1.767613  | -1.327205  | 2.397549  |
| Cl   | 0.214327   | 1.383022   | 1.146093  |
| C    | 2.162883   | -0.634473  | 0.343777  |
| C    | 3.180624   | 0.184510   | 1.013673  |
| H    | 0.716083   | 0.274079   | -1.317124 |
| H    | 2.179294   | -2.709028  | -0.255792 |
| H    | -0.128100  | -3.641993  | 2.063175  |
| H    | 0.829539   | -3.970997  | 0.620821  |
| H    | -0.780099  | -4.655571  | 0.772921  |
| H    | 0.492440   | -3.909684  | -1.757534 |
| H    | 0.186387   | -2.669673  | -2.970630 |
| H    | -1.076299  | -3.830445  | -2.559082 |
| H    | -2.074972  | 0.469986   | -2.636438 |
| H    | -2.792587  | -1.080648  | -3.080990 |
| H    | -1.082102  | -0.777413  | -3.381219 |
| H    | -2.403600  | 1.192996   | 0.909141  |
| H    | -3.823974  | 0.214593   | 0.506535  |
| H    | -2.983367  | 1.124756   | -0.753823 |
| H    | -2.830762  | -1.481928  | 2.607408  |
| H    | -1.509333  | -0.312505  | 2.711449  |
| H    | -1.199912  | -2.022772  | 3.016065  |
| H    | 2.760944   | 0.619201   | 1.924069  |
| H    | 3.361213   | 1.048014   | 0.358247  |
| C    | 4.472980   | -0.568443  | 1.274686  |
| H    | 4.909116   | -0.937012  | 0.343860  |
| H    | 4.300617   | -1.430701  | 1.922489  |
| H    | 5.206645   | 0.073624   | 1.764111  |
TS_C2-12

C  -1.248306  -1.195146  0.925618
C  -0.540423  -2.291365  0.407448
C  -0.769957  -2.334326 -1.014061
C  -1.725240  -1.321809  0.540423
C  -1.979920  -2.291365 -0.366832
Ru  0.237291  -0.381906  0.638652
C  2.068465  -0.725073  0.407448
H  2.549507   0.110199  2.201035
C  0.290192  -3.263690  1.694443
C  -0.261410  -3.381218  1.936227
C  -2.333171  -1.115183  2.684647
C  -2.906105  -0.566832  0.006202
C  -1.314619  -0.734071  2.334427
Cl  0.330220  1.764020  0.433655
C  2.020488  -0.736547 -0.298410
C  2.910895  -0.831366  0.858838
H  0.525830  0.556611 -1.924274
H  2.115853  -1.658153  2.586677
H  0.679388  -2.832903  2.099210
H  1.141957  -3.612806  0.577446
H  -0.295901  -4.147177  1.436988
H  0.737636  -3.720146 -1.654717
H  -0.205240  -3.013895  2.964293
H  -0.913754  -4.260431  1.936487
H  -2.675864  -0.088477 -2.814366
H  -3.194216  -0.775722  2.828425
H  -1.619337  -1.324611  3.482453
H  -2.419826  1.387133  0.526916
H  -3.793842  0.272373  0.562516
H  -3.239275  0.951802 -0.970338
H  -2.319317  0.873719  2.745496
H  -1.070476  0.329863  2.402936
H  -0.616863  -1.280234  2.970709
H  2.329677  -0.827936  1.786151
C  3.845691  0.308633  0.827000
H  3.499116  -1.756519  0.817867
H  3.262133  1.302906  0.839040
H  4.462927  0.372302  -0.072783
H  4.502460  0.371027  1.697026
**TS\textsubscript{C2-E2}**

Ru 0.084553 -0.157825 -0.162085
Cl 1.110585 -2.200838 -0.817647
C 1.943961 0.794189 -0.499449
C 3.100345 0.615500 -0.649957
H 4.012923 1.135835 -0.073753
H 2.455720 -0.318570 0.699957
C 3.200208 -0.177119 1.491339
C 2.043420 1.683369 -1.703868
C -1.726327 0.825587 -0.659735
C -1.122680 1.523000 0.432876
C -0.976728 0.586465 1.500696
C -1.579044 -0.668672 1.091902
C -2.052095 -0.516218 -0.231362
C -2.048256 1.394716 -1.992099
H -1.955848 0.639387 -2.774657
H -1.379478 2.218608 -2.247654
H -3.074435 1.777248 -2.022133
C -0.733141 2.956356 0.466978
H -0.543839 3.109687 -0.535544
H 0.174853 3.109687 1.055125
H -1.520749 3.574212 0.910624
C -0.407470 0.870619 2.841835
H 0.066277 -0.016195 3.267508
H -1.183071 1.197844 3.543255
H 0.347274 1.658272 2.791900
C -1.634632 -1.894388 1.927372
H -1.737800 -2.789026 1.312625
H -2.474692 -1.864173 2.628959
H -0.717883 -2.010565 2.510411
C -2.698460 -1.551614 -1.077034
H -2.346783 -1.490151 -2.109217
H -3.787775 -1.441270 -1.088242
H -2.464590 -2.555739 -0.721537
H 1.594847 1.213120 -2.581021
H 3.069186 1.987623 -1.946750
H 1.463216 2.588597 -1.506631
H 2.329247 -0.824468 1.617947
H 3.229731 0.515655 2.338960
H 4.113710 -0.773186 1.529564
XYZ coordinates (Å) for the molecules present in the hydrogenation of the actual substrate using the neutral catalyst

Alkyne 8b

O  2.196052000  -1.006168000  -0.134210000
O -2.905270000  -0.172328000  1.369312000
H -2.399116000  -0.853764000  1.822197000
C  -0.980049000  0.063820000  0.006137000
C  0.216604000  0.149225000  -0.001352000
C  1.672858000  0.312776000  -0.003894000
C  3.583181000  -1.147331000  -0.041105000
H  3.807926000  -2.190328000  -0.265312000
H  3.964502000  -0.926788000  0.963898000
H  4.126257000  -0.522904000  -0.761963000
C -2.439042000  -0.096411000  0.028097000
C -3.120459000  1.118013000  -0.571746000
H -4.202786000  0.987575000  -0.510812000
H -2.833705000  1.242184000  -1.616800000
H -2.844430000  2.016091000  -0.018690000
C -2.822207000  -1.361351000  -0.727026000
H -2.350194000  -2.235194000  -0.272212000
H -2.501089000  -1.307537000  -1.769044000
H -3.906319000  -1.486722000  -0.690661000
C  2.071202000  1.180483000  -1.193268000
H  3.145821000  1.373223000  -1.198788000
H  1.558063000  2.141911000  -1.140495000
H  1.792365000  0.686775000  -2.125041000
C  2.102379000  0.965044000  1.305536000
H  3.170604000  1.191231000  1.302360000
H  1.879505000  0.360440000  2.146383000
H  1.559526000  1.900574000  1.445902000
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| Ru      | -0.628357    | 0.327766     | -0.384171    |
| Cl      | -0.585830    | 1.164013     | -2.322059    |
| O       | 2.955407     | -2.021336    | 0.236171     |
| O       | -0.189732    | 3.057793     | 0.249033     |
| H       | -0.539161    | 2.768863     | -0.612965    |
| C       | 0.926133     | 0.940663     | 0.233526     |
| C       | 1.610280     | -0.148785    | 3.057753     |
| O       | -0.189732    | 3.057793     | 0.249033     |
| H       | 0.926133     | 0.940663     | 0.233526     |
| C       | 4.040028     | -2.834259    | -0.104418    |
| H       | 3.892897     | -3.787769    | 0.403459     |
| H       | 5.001705     | -2.421809    | 0.226128     |
| C       | 4.098178     | -3.027209    | -1.182275    |
| C       | 1.064866     | 2.422308     | 1.913046     |
| H       | 1.579742     | 3.841348     | 1.913046     |
| C       | 2.552956     | 2.354857     | 1.963812     |
| H       | 0.882793     | 2.342866     | 2.551333     |
| C       | 2.021691     | 2.990418     | -0.648102    |
| H       | 1.659534     | 2.761494     | -1.651734    |
| H       | 3.032594     | 2.593014     | -0.541106    |
| C       | 3.287987     | -0.517044    | -1.656986    |
| H       | 4.293955     | -0.859973    | -1.910368    |
| H       | 3.196735     | 0.527726     | -1.957028    |
| C       | 2.555708     | -1.093012    | -2.230529    |
| C       | 4.021591     | 0.094305     | 0.678094     |
| H       | 5.030457     | -0.281404    | 0.495087     |
| H       | 3.786160     | -0.029576    | 1.736656     |
| C       | 4.023100     | 1.158315     | 0.441383     |
| C       | 2.654827     | 0.319599     | 0.279564     |
| C       | -1.902054    | 0.183611     | 1.473890     |
| C       | -1.387486    | -1.143057    | 1.525175     |
| C       | -1.904529    | -1.869366    | 0.394918     |
| C       | -2.684855    | -0.954815    | -0.388567    |
| C       | -3.391787    | 1.525731     | -0.170948    |
| H       | -3.199920    | 1.726652     | -1.227289    |
| H       | -3.100790    | 2.409115     | 0.397509     |
| H       | -4.469729    | 1.380545     | -0.048275    |
| C       | -1.722674    | 1.236357     | 2.505291     |
| H       | -1.501577    | 2.203889     | 2.052034     |
| H       | -0.914890    | 0.987963     | 3.194870     |
| H       | -2.638485    | 1.335210     | 3.096533     |
| C       | -0.522249    | -1.696064    | 2.599312     |
| H       | 0.017740     | -2.580150    | 2.256584     |
| H       | -1.107652    | -1.979670    | 3.479090     |
| H       | 0.224582     | -0.964810    | 2.918412     |
| C       | -1.742691    | -3.329491    | 0.161874     |
| H       | -1.911704    | -3.584217    | -0.884555    |
| H       | -2.451941    | -3.901814    | 0.767825     |
| H       | -0.736895    | -3.665375    | 0.420057     |
| C       | -3.488019    | -1.243825    | -1.604273    |
| H       | -3.345847    | 0.463816     | 2.354545     |
| H       | -4.555506    | -1.293606    | -1.366476    |
| H       | -3.198240    | -2.191878    | -2.057956    |
| H       | -0.496745    | -1.341697    | -1.616794    |
| H       | 0.961716     | -1.143941    | -0.034912    |
| Element | x                  | y                  | z                  |
|---------|--------------------|--------------------|--------------------|
| Ru      | -0.555269000       | 0.214441000        | -0.058528000       |
| Cl      | -1.612802000       | 2.243314000        | -0.912994000       |
| O       | 0.652760000        | 3.582855000        | 0.544779000        |
| H       | -0.178210000       | 3.406632000        | 0.070920000        |
| C       | 1.026731000        | 1.210325000        | 0.186005000        |
| C       | 1.479954000        | -0.078151000       | 0.538872000        |
| C       | 2.666668000        | 2.710024000        | 1.252924000        |
| H       | 0.432862000        | 0.638599000        | -1.320939000       |
| H       | 1.601222000        | -0.226614000       | 1.617380000        |
| C       | 2.533200000        | -0.920467000       | 1.980302000        |
| C       | 3.549079000        | 2.117648000        | 1.020121000        |
| C       | 2.165040000        | 2.923993000        | -1.190015000       |
| H       | 2.596699000        | 3.927924000        | -1.168460000       |
| C       | 2.375255000        | -0.987141000       | -1.693170000       |
| H       | 3.198294000        | -1.546532000       | -2.141070000       |
| C       | 2.390520000        | 0.016622000        | -2.118690000       |
| H       | 1.431186000        | -1.449976000       | -1.980302000       |
| C       | 3.916585000        | -0.373976000       | 0.153094000        |
| C       | 4.701454000        | -1.038440000       | -0.214683000       |
| H       | 4.033959000        | -0.267120000       | 1.233466000        |
| C       | 4.074277000        | 0.598081000        | -0.316275000       |
| C       | -2.802799000       | -0.407588000       | 0.011797000        |
| C       | -2.194680000       | -0.545315000       | 1.294716000        |
| C       | -1.155546000       | -1.506514000       | 1.171261000        |
| C       | -1.113082000       | -1.993207000       | -0.207597000       |
| C       | -2.128433000       | -1.236555000       | -0.914759000       |
| C       | -4.011205000       | 0.401240000        | -0.261809000       |
| H       | -4.111830000       | 0.646298000        | -1.318022000       |
| H       | -4.012143000       | 1.335520000        | 0.298411000        |
| H       | -4.891935000       | -0.176175000       | 0.040758000        |
| C       | -2.640365000       | 0.151968000        | 2.528368000        |
| H       | -2.832589000       | 1.200999000        | 2.334263000        |
| H       | -1.886544000       | 0.093639000        | 3.313834000        |
| H       | -3.564471000       | -0.286781000       | 2.919681000        |
| C       | -0.370175000       | -2.075532000       | 2.294355000        |
| H       | 0.584546000        | -2.475888000       | 1.953000000        |
| C       | -0.931705000       | -2.879890000       | 2.779650000        |
| H       | -0.162469000       | -1.319544000       | 3.054997000        |
| C       | -0.380370000       | -3.116869000       | -0.734814000       |
| H       | -0.086226000       | -2.985653000       | -1.777758000       |
| H       | -1.031552000       | -3.996152000       | -0.694548000       |
| H       | 0.514567000        | -3.324281000       | -0.154228000       |
| C       | -2.447808000       | -1.367024000       | -2.359656000       |
| H       | -2.725113000       | -0.401134000       | -2.785891000       |
| H       | -3.278240000       | -2.059595000       | -2.529567000       |
| O       | -1.587464000       | -1.735680000       | -2.920575000       |
| C       | 2.402697000        | -2.212196000       | 0.423954000        |
| C       | 3.151775000       | -3.267583000       | -0.100427000       |
| H       | 4.227561000        | -3.058037000       | -0.137428000       |
| H       | 3.001791000        | -4.121640000       | 0.562532000        |
| H       | 2.823582000        | -3.559590000       | -1.106860000       |

**TSE1-E2**
XYZ coordinates (Å) for the molecules for the hydrogenation of 2-butyne using the cationic catalyst

A0
S103
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Ru      | 0.060654000 | -0.226652000 | -0.018922000 |
| C       | 0.375599000 | -2.447578000 | 0.092473000 |
| C       | -0.944332000 | -2.257945000 | -0.542679000 |
| H       | -1.684375000 | -2.306256000 | 0.542679000 |
| H       | 1.068836000 | -2.712729000 | -0.705239000 |
| C       | -1.440536000 | -2.485928000 | 1.489916000 |
| C       | -0.085976000 | -2.437755000 | 2.227297000 |
| H       | -1.777278000 | -2.257786000 | 1.737172000 |
| H       | 0.984462000 | -3.819109000 | 1.610209000 |
| H       | -0.657564000 | -2.299306000 | -2.382247000 |
| H       | -2.300882000 | -1.866211000 | -1.895581000 |
| C       | -1.757842000 | -3.527368000 | -1.756598000 |
| C       | -0.058288000 | 1.731497000 | 0.856935000 |
| C       | -1.163474000 | 0.918814000 | 1.304240000 |
| C       | -1.967174000 | 0.588138000 | 0.172890000 |
| C       | -3.314674000 | 1.120233000 | -0.982111000 |
| C       | -0.149989000 | 1.852880000 | -0.552364000 |
| C       | 0.981325000 | 2.307489000 | 1.744744000 |
| H       | 1.867726000 | 2.609805000 | 1.187154000 |
| H       | 1.292085000 | 1.591670000 | 2.508268000 |
| C       | 0.598491000 | 3.191370000 | 2.265898000 |
| C       | -1.439263000 | 0.554760000 | 2.712686000 |
| H       | -0.515195000 | 0.406940000 | 3.273681000 |
| H       | -2.031777000 | -0.358082000 | 2.785090000 |
| H       | -1.999004000 | 1.351986000 | 3.212218000 |
| C       | -3.299086000 | -0.064526000 | 0.216668000 |
| H       | -3.527284000 | -0.610400000 | -0.698417000 |
| H       | -4.076628000 | 0.694110000 | 0.342253000 |
| H       | -3.389762000 | -0.757756000 | 1.053351000 |
| C       | -1.782583000 | 1.049362000 | -2.385949000 |
| H       | -0.971360000 | 0.774191000 | -3.063241000 |
| H       | -2.153391000 | 2.027878000 | -2.706771000 |
| H       | -2.590215000 | 0.330592000 | -2.515813000 |
| C       | 0.753372000 | 2.601524000 | -1.459962000 |
| H       | 1.709482000 | 2.826152000 | -0.987152000 |
| H       | 0.300530000 | 3.552325000 | -1.755259000 |
| H       | 0.952761000 | 2.037955000 | -2.373797000 |
| C       | 3.274967000 | -0.228953000 | -0.374764000 |
| N       | 2.136837000 | -0.274507000 | -0.240760600 |
| C       | 4.703766000 | -0.174685000 | -0.544254000 |
| H       | 5.199695000 | -0.364226000 | 0.408721000 |
| H       | 5.024036000 | -0.931763000 | -1.261240000 |
| H       | 5.006024000 | 0.807494000 | -0.909393000 |
TS_{E1-ci}

\[
\begin{array}{cccc}
\text{Ru} & -0.113402000 & 0.217411000 & -0.271894000 \\
C & -0.481462000 & 1.890031000 & 0.517823000 \\
C & -0.137050000 & 2.336872000 & -0.752331000 \\
H & -0.450193000 & 0.351510000 & -1.842120000 \\
H & 0.891642000 & 2.650428000 & -1.934201000 \\
C & -1.170344000 & 3.010800000 & -1.614929000 \\
C & -0.481462000 & 1.890031000 & 0.517823000 \\
C & -1.015361000 & 2.442818000 & 1.752481000 \\
H & -0.430193000 & 0.351510000 & -1.842120000 \\
H & -0.137050000 & 2.336872000 & -0.752331000 \\
H & 0.891642000 & 2.650428000 & -1.934201000 \\
H & -2.170600000 & 2.630709000 & -1.397554000 \\
C & -0.312993000 & 3.161623000 & 2.188989000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.090743000 & -0.028388000 & -0.182416000 \\
H & 0.577525000 & -2.673892000 & 2.819448000 \\
C & 1.607000000 & 0.694002000 & 2.310019000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.577704000 & -3.989244000 & 0.247413000 \\
C & 2.017315000 & -0.028388000 & -0.182416000 \\
C & 2.090743000 & -0.028388000 & -0.182416000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\
C & 0.733300000 & -1.271763000 & 1.215128000 \\
C & 2.017315000 & 1.719700000 & 1.995090000 \\
C & 1.592063000 & -1.134253000 & -0.942284000 \\n\end{array}
\]
C1

Ru  -0.133211000  0.261080000  -0.203896000
C    0.036709000  2.031654000  0.454886000
C    -0.443122000  2.508589000  -0.823981000
H    -0.628936000  0.321316000  -1.713602000
H    0.294645000  2.685254000  -1.539085000
C    -1.843519000  2.785939000  -1.096707000
C    -0.443122000  2.308589000  -0.823881000
H    -0.628936000  0.321316000  -1.713602000
C    0.036709000  2.031654000  0.454886000
H    1.031641000  2.210122000  2.353290000
H    1.511339000  3.391796000  -1.157362000
H    0.294645000  2.685254000  -1.539085000
H    1.031641000  2.210122000  2.353290000
C    1.371181000  -0.774511000  1.227062000
C    2.041200000  -0.132185000  0.136915000
C    1.609768000  -0.747342000  -1.084298000
C    0.659799000  -1.764571000  -0.744512000
C    0.513826000  -1.760632000  0.677433000
C    1.597064000  -0.552014000  2.679502000
H    0.659330000  -0.455587000  3.230200000
H    2.191543000  0.341426000  2.869091000
H    2.140990000  -1.395881000  3.114204000
C    3.137340000  0.867881000  0.222970000
H    3.161468000  1.376677000  1.186204000
H    3.055469000  1.625353000  -0.559496000
H    4.104164000  0.373823000  0.091397000
C    2.176980000  -0.464224000  -2.427565000
H    1.510634000  -0.792842000  -3.224638000
H    3.132470000  -0.981485000  -2.555226000
H    2.361694000  0.603911000  -2.568053000
C    0.008508000  -2.720470000  -1.673624000
H    -1.030201000  -2.910497000  -1.403123000
H    0.527726000  -3.682973000  -1.676462000
H    0.011223000  -2.345278000  -2.702763000
C    -0.344020000  -2.677502000  1.468209000
H    -0.763634000  -2.180508000  2.344687000
H    0.243648000  -3.527611000  1.827253000
H    -1.165210000  -3.079842000  0.874414000
C    -3.236792000  -0.418361000  0.257027000
N    -2.140010000  -0.124848000  0.105134000
C    -4.620113000  -0.771743000  0.445770000
H    -4.985784000  -1.334837000  -0.413798000
H    -4.738658000  -1.378673000  1.344028000
H    -5.221773000  0.132044000  0.551954000
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Ru      | -0.126643000 | 0.285617000 | -0.157897000 |
| C       | 0.402033000  | 1.307718000 | 0.701034000  |
| C       | 0.067711000  | 2.418829000 | -0.544785000 |
| H       | -0.445049000 | 0.535067000 | -1.696681000 |
| H       | -0.157897000 | 2.758236000 | -0.718042000 |
| C       | 1.106077000  | 3.025476000 | 1.398904000  |
| C       | 1.235481000  | 2.396959000 | 1.795521000  |
| H       | -0.445049000 | 0.535067000 | -1.696681000 |
| H       | -0.952025000 | 2.758236000 | -0.718042000 |
| C       | 2.144385000  | 2.866725000 | 1.398904000  |
| H       | 1.136817000  | 4.113402000 | -1.334313000 |
| C       | -0.203066000 | -1.887806000 | 0.536606000  |
| C       | 0.843637000  | -1.251600000 | 1.258309000  |
| C       | 1.793386000  | -0.765859000 | 0.307291000  |
| C       | 1.332955000  | -1.116806000 | -1.004240000 |
| C       | 0.095472000  | -1.829498000 | -0.856671000 |
| C       | -1.378552000 | -2.536440000 | 1.150713000  |
| H       | -2.212270000 | -2.627684000 | 0.451920000  |
| H       | -1.722306000 | -2.022642000 | 2.040013000  |
| C       | -1.119984000 | -3.570970000 | 1.458615000  |
| C       | 0.953410000  | -1.206907000 | 2.736010000  |
| H       | 0.013771000  | -0.910690000 | 3.209188000  |
| H       | 1.728254000  | -0.517020000 | 3.073179000  |
| H       | 1.213678000  | -2.194620000 | 3.131940000  |
| C       | 3.121835000  | -0.168537000 | 0.599239000  |
| H       | 3.402892000  | 0.576570000  | -0.146769000 |
| C       | 3.890761000  | -0.946275000 | 0.581637000  |
| H       | 3.161659000  | 0.302292000  | 1.581082000  |
| C       | 2.097620000  | -0.915745000 | -2.262855000 |
| H       | 1.447860000  | -0.358960000 | -3.136455000 |
| H       | 2.848564000  | -1.702102000 | -2.382306000 |
| H       | 2.622075000  | 0.040758000  | -2.264655000 |
| C       | -0.693378000 | -2.473678000 | -1.940479000 |
| H       | -1.767049000 | -2.374636000 | -1.771313000 |
| H       | -0.469642000 | -3.542530000 | -1.999832000 |
| H       | -0.473467000 | -2.034251000 | -2.913131000 |
| C       | -3.303729000 | 0.691074000  | 0.033976000  |
| N       | -2.165855000 | 0.570245000  | -0.019999000 |
| C       | -4.734143000 | 0.845757000  | 0.101948000  |
| H       | -4.997214000 | 1.558547000  | 0.884493000  |
| H       | -5.120699000 | 1.209188000  | -0.850985000 |
| H       | -5.203980000 | -0.111375000 | 0.329938000  |
| Ru  | -0.0539511000 | 0.311976000 | -0.232662000 |
|-----|---------------|-------------|--------------|
| C   | -0.2574490000 | 2.171025000 | -0.532090000 |
| C   | 1.1259660000  | 2.146425000 | -0.386030000 |
| H   | -0.280003000  | 0.731273000 | -1.782659000 |
| C   | 1.7726360000  | 2.864829000 | 0.761947000  |
| H   | 1.7422880000  | 2.056539000 | -1.280605000 |
| C   | -1.2796600000 | 3.197040000 | -0.707275000 |
| H   | -2.2995600000 | 2.831159000 | -0.617516000 |
| H   | -1.1602620000 | 3.691284000 | -1.677840000 |
| H   | -1.1120470000 | 3.974838000 | 0.048590000  |
| H   | 2.7501010000  | 2.446932000 | 1.007914000  |
| H   | 1.1513710000  | 2.837443000 | 1.659214000  |
| H   | 1.9395660000  | 3.914311000 | 0.496755000  |
| C   | -0.0594810000 | -1.941585000 | 1.1301920000 |
| C   | 0.13422898000 | -0.767667000 | 1.1836970000 |
| C   | 1.9131640000  | -0.764372000 | -0.145874000 |
| C   | 1.0603730000  | -1.535620000 | -0.989947000 |
| C   | -1.1703560000 | -2.796319000 | -0.714479000 |
| H   | -1.4741910000 | -2.528685000 | -1.727174000 |
| H   | -2.0472530000 | -2.732080000 | -0.070242000 |
| H   | -0.8645390000 | -3.849338000 | -0.733148000 |
| C   | -0.7572690000 | -1.777653000 | 2.2829120000 |
| H   | -1.8022670000 | -1.899620000 | 1.9853040000 |
| H   | -0.6934980000 | -1.006774000 | 3.0513980000 |
| C   | -0.4693720000 | -2.726904000 | 2.7441210000 |
| C   | 1.9701340000  | -0.210554000 | 2.4087990000 |
| H   | 2.7039200000  | 0.560854000  | 2.1815530000 |
| H   | 2.4899630000  | -1.002627000 | 2.9561940000 |
| H   | 1.2292890000  | 0.219557000  | 3.0843580000 |
| C   | 3.2621920000  | -0.277936000 | -0.524940000 |
| H   | 3.2866130000  | 0.084796000  | -1.553615000 |
| H   | 3.9873080000  | -1.093995000 | -0.453209000 |
| H   | 3.6109100000  | 0.524389000  | 0.1246410000 |
| C   | 1.3206800000  | -1.864692000 | -2.413233000 |
| H   | 0.3966640000  | -2.047952000 | -2.961519000 |
| H   | 1.9324090000  | -2.768871000 | -2.483736000 |
| H   | 1.8601750000  | -1.064611000 | -2.920631000 |
| C   | -3.2453070000 | 0.175950000  | 0.0839000000 |
| N   | -2.1091890000 | 0.275508000  | -0.024074000 |
| C   | -4.6737800000 | 0.046702000  | 0.2194760000 |
| H   | -5.0278320000 | 0.620903000  | 1.0764580000 |
| H   | -5.1717120000 | 0.409220000  | -0.680694000 |
| H   | -4.9392070000 | -1.001342000 | 0.3656700000 |
TS\textsubscript{A3-Z1}

Ru  -0.10366000  0.024842000  -0.339399000
C  -1.128470000  1.643220000  0.397328000
C  -1.372775000  1.391186000  -0.847150000
H  -0.122514000  0.599016000  -1.821038000
H  -1.290913000  1.175789000  -1.625853000
C  -1.613824000  3.338302000  -1.449623000
C  -1.309971000  2.329306000  1.683299000
C  1.058978000  -0.502877000  1.432044000
C  1.718802000  -1.262166000  -1.625853000
C  1.719809000  -1.262166000  -1.625853000
C  1.033855000  -0.502877000  1.432044000
C  0.562185000  -0.530665000  2.831675000
C  2.115428000  1.894241000  1.313297000
H  1.740555000  -2.179876000  0.692165000
H  1.761111000  1.966468000  1.356707000
C  2.249620000  0.913645000  -0.550723000
H  2.569610900  1.970341000  -1.398108000
H  2.067436000  -2.174154000  -1.778928000
C  1.323537000  -2.959619000  -1.909871000
C  0.493374000  -0.331107000  -0.361078000
H  -0.331107000  -2.912497000  1.56236000
C  1.269581000  -3.597566000  1.302305000
H  0.135719000  -3.482356000  -0.043016000
H  -0.361078000  2.524570000  2.186628000
H  -1.900150000  1.705939000  2.36142000
H  -1.837870000  3.279594000  1.562782000
H  -0.771874000  3.640142000  -2.077172000
H  -1.738929000  4.089460000  -0.669541000
H  -2.503539000  3.340616000  -2.081583000
C  -2.991368000  -1.410028000  -0.267110000
N  -1.975515000  -0.882436000  -0.293248000
C  -4.268991000  -2.075552000  -0.239554000
H  -5.021066000  -1.420620000  0.209569000
H  -4.582653000  -2.327891000  -1.253211000
H  -4.203348000  -2.993446000  0.345690000

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|      | x   | y   | z   |
|------|-----|-----|-----|
| Ru   | -0.059661000 | -0.025859000 | -0.296998000 |
| H    | -0.746329000  | 0.115236000  | -3.072448000 |
| H    | -0.231131000  | 0.491455000  | -2.668473000 |
| C    | -0.590049000  | -1.859795000 | -0.443995000 |
| C    | -1.182128000  | -2.674803000 | 0.652971000  |
| H    | -0.962533000  | -2.320710000 | 1.627970000  |
| H    | -0.781768000  | -3.697697000 | 0.643450000  |
| C    | -2.701162000  | -2.731305000 | 0.478191000  |
| C    | -0.279074000  | -2.649810000 | -1.663303000 |
| H    | 0.497282000   | -3.384661000 | -1.409834000 |
| H    | 0.066798000   | -2.062477000 | -2.513113000 |
| H    | -1.149783000  | -3.243302000 | -1.968439000 |
| H    | -2.981935000  | -3.172052000 | -0.479737000 |
| H    | -3.134413000  | -1.731417000 | 0.533133000  |
| H    | -3.145038000  | -3.339024000 | 1.266380000  |
| C    | 1.618310000   | 1.470068000  | -0.402837000 |
| C    | 2.094838000   | 0.094114000  | -0.447417000 |
| C    | 1.761795000   | -0.530467000 | 0.782422000  |
| C    | 0.960989000   | 0.398705000  | 1.532507000  |
| C    | 0.947890000   | 1.655339000  | 0.809118000  |
| C    | 1.853875000   | 2.474374000  | -1.470081000 |
| H    | 1.132441000   | 3.290636000  | -1.428139000 |
| H    | 1.801113000   | 2.030497000  | -2.465422000 |
| H    | 2.851671000   | 2.911899000  | -1.369052000 |
| C    | 2.907408000   | -0.480564000 | -1.547859000 |
| H    | 2.925287000   | -1.569912000 | -1.511079000 |
| H    | 3.942257000   | -0.129596000 | -1.487651000 |
| H    | 2.523720000   | -0.185513000 | -2.526489000 |
| C    | 2.189368000   | -1.877482000 | 1.238131000  |
| H    | 1.463436000   | -2.331553000 | 1.913688000  |
| H    | 3.135932000   | -1.806890000 | 1.780877000  |
| H    | 2.343800000   | -2.560588000 | 0.401707000  |
| C    | 0.432116000   | 0.204074000  | 2.902971000  |
| H    | -0.528374000  | 0.705123000  | 3.033996000  |
| H    | 1.122729000   | 0.622783000  | 3.642317000  |
| H    | 0.297324000   | -0.850843000 | 3.142732000  |
| C    | 0.271861000   | 2.886581000  | 1.288355000  |
| H    | 0.902735000   | 3.418309000  | 2.006099000  |
| H    | -0.666331000  | 2.654310000  | 1.796294000  |
| H    | 0.051902000   | 3.573895000  | 0.470745000  |
| C    | -2.933153000  | 1.472844000  | -0.380404000 |
| N    | -1.940089000  | 0.900554000  | -0.352126000 |
| C    | -4.184705000  | 2.183398000  | -0.418483000 |
| H    | -4.200166000  | 2.869910000  | -1.266057000 |
| H    | -5.011700000  | 1.479794000  | -0.522141000 |
| H    | -4.322301000  | 2.756632000  | 0.499757000  |
### TSr3-d1

| Atom | X | Y | Z |
|------|---|---|---|
| Ru   | 0.095300000 | 0.211900000 | -0.570700000 |
| C    | -1.362150000 | -1.330550000 | -0.609900000 |
| C    | -2.297664000 | -1.679342000 | 0.516068000 |
| H    | -2.688352000 | -0.756490000 | 0.958973000 |
| H    | -1.742773000 | -2.194716000 | 1.308115000 |
| C    | -3.457065000 | -2.561801000 | 0.075527000 |
| C    | -0.658973000 | -2.495070000 | -1.265421000 |
| H    | -0.251578000 | -3.203609000 | 0.516068000 |
| H    | -0.149900000 | -2.166062000 | -1.932554000 |
| H    | -1.351413000 | -3.046275000 | -0.742363000 |
| C    | 2.237526000 | 0.634841000 | 0.897488000 |
| C    | 2.093570000 | -0.767112000 | -0.036017000 |
| C    | 1.224544000 | -0.945860000 | 1.471542000 |
| C    | 0.753723000 | 0.340860000 | 1.471542000 |
| C    | 1.418991000 | 1.337017000 | 0.653213000 |
| C    | 3.195105000 | 1.221023000 | -1.258774000 |
| H    | 2.964923000 | 2.263188000 | -1.476531000 |
| H    | 3.193763000 | 0.675550000 | -2.202879000 |
| H    | 4.211503000 | 1.177693000 | -0.856349000 |
| H    | -4.151946000 | -2.737360000 | 0.897488000 |
| C    | 2.323752600 | 0.634841000 | -0.285890000 |
| C    | 2.093570000 | -0.767112000 | -0.036017000 |
| C    | 1.224544000 | -0.945860000 | 1.471542000 |
| H    | 3.890513000 | -1.816811000 | -0.448855000 |
| C    | 0.983729000 | -2.215450000 | 1.797237000 |
| H    | 0.058751000 | -2.193858000 | 2.371631000 |
| H    | 1.799567000 | -2.376596000 | 2.508747000 |
| H    | 0.960341000 | -3.083398000 | 1.139014000 |
| C    | -0.126597000 | 0.622176000 | 2.630933000 |
| H    | -0.614608000 | 1.592414000 | 2.538755000 |
| H    | 0.458349000 | 0.638019000 | 3.555812000 |
| H    | -0.901023000 | -0.138130000 | 2.744123000 |
| C    | 1.348357000 | 2.804588000 | 0.856350000 |
| H    | 1.613423000 | 3.348214000 | -0.050187000 |
| H    | 2.036852000 | 3.113694000 | 1.648436000 |
| H    | 0.347565000 | 3.119853000 | 1.153805000 |
| C    | -2.505482000 | 2.068447000 | -0.417279000 |
| N    | -1.587336000 | 1.385530000 | -0.477198000 |
| C    | -3.653588000 | 2.936793000 | -0.354695000 |
| C    | -4.115609000 | 3.014513000 | -1.339050000 |
| H    | -4.389314000 | 2.544447000 | 0.348040000 |
| H    | -3.353392000 | 3.934136000 | -0.031056000 |
| H    | 0.423174000 | 1.367139000 | -1.638058000 |
| H    | -1.914698000 | -0.776609000 | -1.387095000 |
TS\textsubscript{R3-d1}'

\begin{tabular}{cccc}
Ru & -0.106310000 & -0.102817000 & -0.508906000 \\
H  & -0.362160000 & -0.986870000 & -1.827331000 \\
H  & -1.399342000 & 1.855000000 & -0.880004000 \\
C  & -0.661054000 & 1.900419000 & -0.056290000 \\
C  & 0.501727000 & 2.740791000 & -0.520629000 \\
H  & 1.053813000 & 2.207355000 & 1.087291000 \\
H  & 1.205602000 & 2.908097000 & 1.399342000 \\
\end{tabular}
| Atom | X-coordinate | Y-coordinate | Z-coordinate |
|------|--------------|--------------|--------------|
| Ru   | -0.119872000 | 0.116736000  | -0.325741000 |
| H    | -0.536933000 | -0.367785000 | -0.778038000 |
| C    | -1.852899000 | 1.719585000  | 1.000162000  |
| C    | -0.842210000 | 1.904127000  | 0.636615000  |
| C    | -0.801623000 | 2.309441000  | -0.325741000 |
| H    | -0.358093000 | 1.456791000  | -1.497760000 |
| H    | -0.029913000 | 3.066548000  | -0.949784000 |
| C    | -2.117799000 | 2.655973000  | -1.442101000 |
| C    | -0.039153000 | 2.714607000  | 1.605141000  |
| C    | 0.980563000  | 2.880260000  | 1.254551000  |
| C    | 0.003585000  | 2.261155000  | 2.595012000  |
| H    | -0.505068000 | 3.695550000  | 1.731891000  |
| H    | -2.516467000 | 1.864432000  | -1.286472000 |
| H    | -2.851929000 | 2.809597000  | -2.515726000 |
| C    | 0.973778000  | -1.755477000 | -0.452886000 |
| C    | 0.800565000  | -1.463744000 | 0.941981000  |
| C    | 1.519856000  | -0.280124000 | 1.250150000  |
| C    | 2.075733000  | 0.225085000  | 0.035864000  |
| C    | 1.770097000  | -0.702844000 | -1.014444000 |
| C    | 0.512212000  | -2.923820000 | -1.135030000 |
| H    | -0.503379000 | -2.873562000 | -2.218166000 |
| H    | -0.497884000 | -3.268272000 | -0.825850000 |
| H    | 1.170160000  | -3.821960000 | -0.894736000 |
| C    | 0.086827000  | -2.314682000 | 1.925952000  |
| H    | -0.433081000 | -1.714339000 | 2.674355000  |
| H    | 0.796232000  | -2.957117000 | 2.456148000  |
| C    | -0.642509000 | -2.964668000 | 1.442459000  |
| C    | 1.745186000  | 0.224909000  | 2.625423000  |
| H    | 2.114226000  | 1.248279000  | 2.644223000  |
| C    | 2.495865000  | -0.402300000 | 3.116260000  |
| H    | 0.841035000  | 0.175949000  | 3.234349000  |
| C    | 3.973904000  | 1.399103000  | -0.123869000 |
| H    | 2.693468000  | 2.008715000  | -0.983474000 |
| H    | 4.003780000  | 1.068928000  | -0.285567000 |
| H    | 2.972755000  | 2.040743000  | 0.758455000  |
| C    | 2.316905000  | -0.631883000 | -2.393882000 |
| C    | 3.338284000  | -1.023096000 | -2.416042000 |
| H    | 2.353911000  | 0.395688000  | -2.757809000 |
| C    | 1.721427000  | -1.212799000 | -3.097988000 |
| C    | -3.124253000 | 0.923407000  | 0.138659000  |
| N    | -2.071322000 | 0.504240000  | -0.029737000 |
| C    | -4.449683000 | 1.451718000  | 0.341529000  |
| H    | -4.403945000 | -2.368018000 | 0.931293000  |
| H    | -5.067228000 | -0.725923000 | 0.871766000  |
| H    | -4.915928000 | -1.675420000 | -0.618798000 |
### D3'

| Atom | x       | y       | z       |
|------|---------|---------|---------|
| Ru   | -0.019862000 | 0.144072000 | -0.404219000 |
| H    | -0.222981000 | 0.754326000 | -2.194625000 |
| H    | -1.195243000 | 2.641487000 | -0.921747000 |
| C    | -0.547469000 | 2.375538000 | -0.086648000 |
| C    | 0.803236000 | 2.289718000 | -0.357097000 |
| H    | -0.003171000 | -0.044852000 | -2.172001000 |
| H    | 1.469516000 | 2.305538000 | 0.502074000 |
| C    | 1.123659000 | 2.627744000 | 1.266744000 |
| H    | -0.433779000 | 2.341202000 | -1.762268000 |
| H    | -2.066080000 | 2.099007000 | 1.420888000 |
| C    | -1.395706000 | 3.694897000 | 1.387856000 |
| C    | 1.879788000 | 3.700377000 | -1.530058000 |
| H    | 0.701343000 | 2.770422000 | -2.453259000 |
| H    | 2.233763000 | 2.032981000 | -1.958240000 |
| C    | 1.429030000 | -1.527909000 | -0.524485000 |
| C    | 0.205012000 | -1.976395000 | 0.054816000 |
| C    | 0.013457000 | -1.243142000 | 1.282778000 |
| C    | 1.101302000 | -0.345356000 | 1.434973000 |
| C    | 1.971938000 | -0.498740000 | 0.297094000 |
| C    | 2.058813000 | -0.252109000 | -1.762268000 |
| H    | 2.581559000 | -1.267174000 | -2.310891000 |
| H    | 1.395706000 | -2.506771000 | -2.432433000 |
| H    | 2.796237000 | -2.819287000 | -1.509263000 |
| C    | -0.650840000 | -3.084541000 | -0.441633000 |
| H    | -1.701439000 | -2.922089000 | -0.197880000 |
| H    | -0.355945000 | -4.036639000 | 0.008710000 |
| H    | -0.576792000 | -3.195793000 | -1.523989000 |
| C    | -1.087061000 | -1.446877000 | 2.257469000 |
| H    | -1.376262000 | -0.510881000 | 2.738124000 |
| H    | -0.776668000 | -2.140264000 | 3.044310000 |
| H    | -1.972833000 | -1.869985000 | 1.783535000 |
| C    | 1.397299000 | 0.463402000 | 2.643279000 |
| H    | 1.856388000 | 1.425080000 | 2.410470000 |
| H    | 2.107135000 | -0.079447000 | 3.275010000 |
| H    | 0.506057000 | 0.647453000 | 3.243086000 |
| C    | 3.312563000 | 0.117971000 | 0.130724000 |
| H    | 4.076856000 | -0.511530000 | 0.596474000 |
| H    | 3.397815000 | 1.101008000 | 0.597097000 |
| H    | 3.582746000 | 0.227800000 | -0.920477000 |
| C    | -3.248361000 | -0.004702000 | -0.584766000 |
| N    | -2.106010000 | 0.087271000 | -0.524898000 |
| C    | -4.683980000 | -0.123025000 | -0.609415000 |
| H    | -5.032161000 | -0.816309000 | 0.157238000 |
| H    | -5.149364000 | 0.848524000 | -0.439501000 |
| H    | -4.995849000 | -0.495361000 | -1.586075000 |
| At.  | X        | Y        | Z        |
|------|----------|----------|----------|
| Ru   | -0.066267| 0.194692 | 0.041908 |
| H    | 0.255390 | 0.774802 | -1.399724|
| C    | 1.179469 | 2.571800 | -0.417824|
| C    | 1.504287 | 1.620533 | 0.004421 |
| C    | 2.864270 | 1.223226 | -0.496370|
| C    | 2.818552 | 1.053100 | -1.576659|
| C    | 3.159294 | 0.270514 | -0.041839|
| C    | 3.908351 | 2.284280 | -0.188565|
| C    | 1.254197 | 1.528876 | 1.462664 |
| C    | 0.533164 | -1.627808| 0.984481 |
| C    | -0.887528| -1.395695| -1.153825|
| C    | -2.981377| -1.468746| 0.369591 |
| H    | -3.450242| -0.718720| -0.269260|
| H    | -3.210819| -1.223621| 1.406633 |
| H    | -3.458407| -2.426633| 0.142920 |
| C    | -0.690860| -1.988577| 2.539310 |
| C    | 0.126599 | -1.550328| 0.128004 |
| C    | -0.051636| -1.769862| 1.081054 |
| C    | 0.768823 | -1.805463| 0.400988 |
| C    | 0.533164 | -1.627808| 0.984481 |
| C    | -0.887528| -1.395695| -1.153825|
| C    | -2.981377| -1.468746| 0.369591 |
| H    | -3.450242| -0.718720| -0.269260|
| H    | -3.210819| -1.223621| 1.406633 |
| H    | -3.458407| -2.426633| 0.142920 |
| C    | -0.690860| -1.988577| 2.539310 |
| C    | 0.126599 | -1.550328| 0.128004 |
| C    | -0.051636| -1.769862| 1.081054 |
| H    | -1.626841| -1.567708| 2.906263 |
| C    | 2.056357 | -2.154879| 1.054394 |
| H    | 2.908175 | -1.967066| 0.401555 |
| H    | 2.071522 | -3.216994| 1.316379 |
| H    | 2.212020 | -1.596633| 1.980112 |
| C    | 1.526517 | -1.755135| -2.078106|
| C    | 1.274175 | -1.123408| -2.930234|
| H    | 1.563502 | -2.789168| 2.432154 |
| H    | 2.529442 | -1.484166| -1.748756|
| C    | -1.608910| -1.249635| -2.443720|
| H    | -2.011568| -2.212829| -2.770568|
| H    | -0.953481| -0.878019| -3.231077|
| H    | -2.447310| -0.556822| -2.355049|
| C    | -2.199941| 2.607970 | 0.000541 |
| N    | -1.433744| 1.749796 | 0.038668 |
| C    | -3.166529| 3.668435 | -0.053214|
| H    | -4.120397| 3.336045| 0.357927 |
| H    | -2.814825| 4.523621| 0.525054 |
| H    | -3.318672| 3.984145| -1.086157|

S141
TsB1'-B2'

Ru   0.0625220000  0.17885000  -0.0697110000
H   -0.4705310000  0.8736490000  1.2639130000
H   -1.2289580000  2.5852950000  0.3961060000
C   -1.5309740000  1.6147740000  0.0005600000
C   -2.8914290000  1.2104990000  1.5860690000
H   -2.8560460000  1.0687810000  0.0689420000
H   -3.3674500000  0.2410570000  0.0689420000
C   -4.9461410000  2.2476410000  0.1544440000
C   -3.1923200000  1.5088450000  -1.4637990000
H   -3.1120530000  1.0265970000  -1.3978290000
H   -3.6930800000  0.8648880000  -1.7750790000
H   -4.0352500000  2.4534570000  -1.9336200000
C   -3.6967340000  0.3961060000  0.5871900000
C   -4.9265410000  2.3798100000  -0.9267040000
H   -4.9265410000  1.9579030000  0.5335240000
C   -0.7352300000  -1.8427070000  -0.3707600000
C   -0.4982670000  -1.6236780000  1.0104600000
C   0.9100300000  -1.3488300000  1.1752530000
C   3.0025040000  -1.3976550000  -0.3573870000
H   3.4588720000  -0.6391020000  0.2801600000
H   3.2197000000  -1.1443020000  -1.3952340000
H   3.5016710000  -2.3455790000  -0.1369240000
C   0.7237380000  -2.0326570000  -2.5066410000
H   -0.1041660000  -1.6297560000  -3.0924820000
H   0.7600980000  -3.1080560000  -2.7054080000
H   1.6493450000  -1.5972120000  -2.8826840000
C   -2.0182380000  -2.2279980000  -1.0133510000
H   -2.8711650000  -2.0428660000  -0.3608080000
H   -3.0178340000  -3.2942160000  -1.2578110000
H   -3.1862280000  -1.6862940000  -1.9469950000
C   -1.4926250000  -1.7333680000  2.1069870000
H   -1.2502080000  -1.0726410000  2.9399600000
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H   -2.5002150000  -1.4901080000  1.7700130000
C   1.6234490000  -1.1426370000  2.4612380000
H   2.0283480000  -2.0871450000  2.8364450000
H   0.9613900000  -0.7375060000  3.2265020000
H   2.4591130000  -0.4505110000  2.3461260000
C   2.1729740000  2.6122980000  -0.0148150000
N   1.4118420000  1.7557930000  -0.0534550000
C   3.1347890000  3.6837840000  0.0382260000
H   4.0333270000  3.4135450000  -0.5176980000
H   2.7124760000  4.5898910000  -0.3977150000
H   3.4097590000  3.8899500000  1.0734470000
|   | \text{Ru}  | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   | \text{H}   | \text{C}   |
|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|   | -0.132339| 0.133782 | 0.136232 | 0.236225 | -0.125036| 0.675730 | -0.471962 | -1.098871| -0.847107 | 0.645647  | 0.610535  | 0.707488  | 1.737007  | 1.786669  | 0.736066  | 0.070772  |
|   | 0.067894 | 1.891467 | 3.176376 | 3.442724 | 1.374991  | 1.315873 | -0.342922 | 1.567384 | 3.442480  | 2.679243  | 4.412134  | -2.031751 | -1.061347 | -0.165925 | -0.512674 | -1.660443 |
|   | 0.460522 | 0.067894 | 0.344778 | -0.125036| 2.159994  | 2.897917 | 1.977561  | 2.610828 | -1.235250 | -1.764189 | -1.426003 | 0.189089  | 0.441282  | -0.685147 | -1.572989 | -1.015016 |
|   | 0.067894 | 0.067894 | 0.879509 | 0.969360  | 0.487100  | 0.879509 | 0.487100  | 0.969360 | 0.487100  | 0.879509  | 0.487100  | 0.879509  | 0.487100  | 0.879509  | 0.487100  | 0.879509  |
|   | 0.067894 | 0.067894 | 0.344778 | -0.125036| 2.159994  | 2.897917 | 1.977561  | 2.610828 | -1.235250 | -1.764189 | -1.426003 | 0.189089  | 0.441282  | -0.685147 | -1.572989 | -1.015016 |
|   | 0.067894 | 0.067894 | 0.344778 | -0.125036| 2.159994  | 2.897917 | 1.977561  | 2.610828 | -1.235250 | -1.764189 | -1.426003 | 0.189089  | 0.441282  | -0.685147 | -1.572989 | -1.015016 |
|   | 0.067894 | 0.067894 | 0.344778 | -0.125036| 2.159994  | 2.897917 | 1.977561  | 2.610828 | -1.235250 | -1.764189 | -1.426003 | 0.189089  | 0.441282  | -0.685147 | -1.572989 | -1.015016 |

**TSc2-11**
|   | Ru     | C   | H   | C   | C   | H   | C   | C   | H   | C   | H   | C   | C   | H   | C   |
|---|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 0.025952000 | 0.008788000 | -0.562389000 |
|   | 0.497621000 | 1.810381000 | -0.909240000 |
|   | 1.144725000 | 2.566649000 | -0.293537000 |
| H | 0.365200000 | 3.737644000 | -0.186316000 |
| H | 1.806532000 | 3.911960000 | -1.060431000 |
| C | 1.875778000 | 2.728860000 | 1.010344000 |
| C | -0.117583000 | 1.489203000 | -2.107706000 |
| H | -1.142860000 | 1.800474000 | -1.060431000 |
| H | 0.069493000 | 0.719911000 | -1.986774000 |
| H | 0.489924000 | 1.418250000 | -3.007662000 |
| H | 2.658573000 | 1.970837000 | 0.886375000 |
| H | 1.196804000 | 2.370577000 | 1.784890000 |
| H | 2.340886000 | 3.664360000 | 1.369342000 |
| C | -0.689407000 | -1.142860000 | -2.307356000 |
| C | -1.700548000 | -1.419675000 | -0.147267000 |
| C | -2.129618000 | -0.057824000 | -0.049522000 |
| C | -1.460454000 | 0.540814000 | 1.080995000 |
| C | -0.551946000 | -0.401378000 | 1.602943000 |
| H | 0.035991000 | -2.882247000 | 1.096707000 |
| H | 1.028148000 | -2.694813000 | 1.509620000 |
| H | 0.452596000 | -3.486468000 | 0.196071000 |
| H | -0.509145000 | -3.489924000 | 1.829545000 |
| C | -2.254615000 | -2.437178000 | -1.076055000 |
| H | -1.536553000 | -3.229974000 | -1.284673000 |
| H | -2.551859000 | -1.996143000 | -2.027497000 |
| H | -3.142048000 | -2.901691000 | -0.636518000 |
| C | -3.235158000 | 0.550921000 | -0.825332000 |
| H | -3.128418000 | 1.643955000 | -0.895840000 |
| H | -4.198151000 | 0.363214000 | -0.344832000 |
| H | -3.286676000 | 0.160728000 | -1.839379000 |
| C | -1.778795000 | 1.891540000 | 1.614622000 |
| H | -0.996491000 | 2.270941000 | 2.271625000 |
| H | -2.705943000 | 1.857459000 | 2.194670000 |
| H | -1.933308000 | 2.619415000 | 0.815315000 |
| C | 0.303914000 | -0.273509000 | 2.811570000 |
| H | 1.343577000 | -0.538440000 | 2.605041000 |
| H | -0.047633000 | -0.940138000 | 3.604321000 |
| H | 0.294354000 | 0.740645000 | 3.210274000 |
| C | 3.047597000 | -1.068502000 | -0.449593000 |
| N | 1.987111000 | -0.638660000 | -0.494707000 |
| C | 4.381599000 | -1.610891000 | -0.407906000 |
| H | 4.693953000 | -1.916788000 | -1.407291000 |
| H | 5.082673000 | -1.864787000 | -0.031989000 |
| H | 4.411308000 | -2.480820000 | 0.249376000 |
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Figure S-1. Structure of the ruthenium carbene 9b (R = Me) in the solid state, showing the two independent molecules in the unit cell; hydrogen atoms are omitted for clarity, except those of the –OH group and the –CH₂- group flanking the carbene center; color code: Ru = blue, O = red, Cl = green

Figure S-2. Different projection showing one of the two independent molecules of ruthenium carbene 9b (R = Me) present in the unit cell; hydrogen atoms are omitted for clarity, except the one on O1 involved in hydrogen bonding with Cl1 and the geminal H-atoms at C2 flanking the carbene center C1; color code: Ru = blue, O = red, Cl = green
X-ray Crystal Structure Analysis of Complex 9b: C_{19}H_{33}ClO_2Ru, M_r = 429.97 g · mol^{-1}, orange block, crystal size 0.18 x 0.10 x 0.02 mm, triclinic, space group P\overline{1}, a = 9.1699(13) Å, b = 14.0446(13) Å, c = 15.7493(16) Å, α = 86.283(10), β = 89.332(10), γ = 83.746(10), V = 2012.0(4) Å³, T = 100 K, Z = 4, \( D_{\text{calc}} = 1.419 \text{ g·cm}^{-3}, \lambda = 0.71073 \text{ Å}, \mu(\text{Mo-K}α) = 0.919 \text{ mm}^{-1}, \) Gaussian absorption correction (\( T_{\text{min}} = 0.85, T_{\text{max}} = 0.98), \) Bruker-AXS Smart APEX-II diffractometer, 2.799 < 2θ < 32.032°, 39856 measured reflections, 13943 independent reflections, 10867 reflections with \( I > 2\sigma(I), \) Structure solved by direct methods and refined by full-matrix least-squares against \( F^2 \) to \( R_1 = 0.038 [I > 2\sigma(I)], wR_2 = 0.099, 437 \) parameters, H atoms riding, \( S = 1.019, \) residual electron density 1.5 / -1.5 e Å^{-3}.

CCDC 1406683 contains the supporting crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
NMR INVESTIGATIONS

**General.** The CD$_2$Cl$_2$ used in these experiments was dried by distillation over CaCO$_3$ and stored in a Schlenk-flask in a glovebox. Unless stated otherwise, all commercially available compounds were used as received and stored under argon. [Cp*Ru(CH$_3$CN)$_3$]PF$_6$ was prepared according to a literature procedure.$^{[1]}$ [Cp*Ru(cod)Cl] was purchased from Strem.

**Sample Preparation.** All samples were prepared in a glovebox. The substrate (0.1 mmol) and the catalyst (5.5 mol%) were dissolved in 0.4 mL CD$_2$Cl$_2$ in a 2 mL GC vial. After transferring the material into the pressure NMR-tube (5 mm medium wall precision pressure/vacuum valve NMR sample tube, Wilmad) via syringe, the tube was connected to the $p$-H$_2$-storage container or directly to the generator. The tubing was flushed with $p$-H$_2$ to ensure that no other gases were present. Then the Swagelok® connection to the NMR tube was tightened and the pressure valve opened to fill the tube with hydrogen. After closing the valve, the tube was shaken and directly transferred into the NMR magnet.

**NMR Measurements.** All spectra were acquired on an Bruker Ascend AVIII 500 MHz NMR spectrometer (11.7 Tesla) equipped with an Bruker 5mm BBFO$^{plus}$ 500 MHz SmartProbe$^TM$ (PA BBO 500S1 BBF-H-D-05 Z Plus) or Bruker 5mm TBI Probe (PH TBI 500S1 H/C-BB-D-05 Z) at 298 K unless otherwise mentioned.

The acquired $^1$H NMR spectra were referenced to the residual solvent signal ($\delta_{\text{CDCl}_3} = 5.32$ ppm)$^{[2]}$. The $^{13}$C NMR spectra were referenced with the $\Xi$-scale.$^{[3,4]}$

For the OPSY-EXSY spectrum, a mixing time of 300 ms was used.

NMR data was processed with Bruker’s Topspin 3.2. For the simulation of the NMR spectra, the DAISY module of Topspin was used. The NMR assignment of the carbenes 9 was performed with MestreNova 9.1.

**para-Hydrogen Generation.** The $p$-H$_2$ enrichment above the thermal equilibrium of 25% was achieved in two different ways.

Initially, the $p$-H$_2$ was enriched to 50% using the “U-shaped tube” method (Figure S-3)$^{[5]}$. The tube was filled with a mixture (3:1) of activated charcoal (Norit PK1-3, Sigma Aldrich) and iron(III) oxide (99%, meshed powder, Alfa Aesar). The filled tube was evacuated and heated with a heat gun (150 °C) to remove any residual water and oxygen from the catalyst. This tube was used several times before the catalyst had to be reactivated. To enrich the $p$-H$_2$, the tube was loaded with 20 bar of hydrogen gas (99.995%, dry) and placed in a Dewar flask filled with liquid nitrogen (77 K). After an equilibration time of 1h, the enriched hydrogen gas was transferred to an evacuated storage bottle or directly transferred to the NMR tube.
An enrichment of approx. 92 % was achieved with the commercially available Parahydrogen pH2 Generator from Bruker BioSpin GmbH.

**2D-EXSY with OPSY Filter.** A 2D-EXSY (Exchange Spectroscopy) experiment was adapted to $p$-H$_2$ induced polarization with an OPSY-d-filter (Figure S-4) to follow chemical exchanges involving the hydrogenated species during the reaction. Typically, experiments were recorded with 512 increments and 2 scans (8k points) per increments. Mixing times of $\tau_{\text{mix}} = 2\tau = 300$ ms were used. Short repetition times of 1.1 s ($\tau_{\text{mix}} + \text{aq}$) allowed for an overall experimental time of 20 min (relaxation delays were unnecessary).
Figure S-4. NOESY/EXSY with OPSY-d-Filter (OPSY-d-EXSY): Black thin bars represent 90° pulses and thick bars represent 180° pulses; pulses are applied with x-phase unless the phase is indicated above the bar. Phase cycle: \( \phi_1 = [x,-x] \), \( \phi_2 = [(x)_d (-x)_d] \), \( \phi_3 = [x,x,-x,y,y,-y,-y] \), \( \phi_{aq} = [x,-x,x,y,y,-y,y,-y] \). Half-sine 1ms gradients were used with gradient ratio \( g_1:g_2:g_3:g_4 = 10:20:4:-4 \), and were each followed by a 0.2 ms recovery delay. The chemical exchange mixing time is represented by \( 2\tau \).

NMR Assignments of the Stable Carbenes. Standard \(^1\text{H},^1\text{H}-\text{NOESY} (t_{\text{mix}} = 1s)\), \(^1\text{H},^{13}\text{C}-\text{HSQC} \) and \(^1\text{H},^{13}\text{C}-\text{HMBC} \) experiments were used for the characterization of the stable carbenes.

Figure S-5. NMR assignments of 9a (a) and 9b (c) and selected connections observed in the 2D NMR spectra (b and d)
Sign of the $J_{\text{HH}}$ Couplings. The shape of the PASADENA antiphase signal gives information about the sign of the coupling constant. In the case of a positive coupling the first signal of the doublet is positive, whereas the second one is negative. This can be seen for the vicinal coupling of the olefinic protons of 5a (Fehler! Verweisquelle konnte nicht gefunden werden., left). If the coupling is negative, the sign of the antiphase signals is inverted. This can be nicely seen in the case the hyperpolarized protons of 7a and 6a proving that the coupling is indeed negative (Figure S1, middle & left). Negative couplings are normally observed for geminal proton-proton couplings.

Figure S-6: Hyperpolarized antiphase signals of 5a, 6a and 7a
Figure S-7: Top: OPSY-d-spectrum during the reaction 4a in the presence of p-H₂ and 2; Bottom: Comparison of the acquired OPSY-Spectrum (black) and the simulated spectrum (green).
The $^1$H-OPSY-COSY spectrum contains various structure informations about the carbene intermediates $6a$ and $7b$. On the one hand it clearly shows the cross peaks between the geminal protons ($H2\alpha \leftrightarrow H2\beta$, $H1\alpha \leftrightarrow H1\beta$). On the other hand asymmetrical cross peaks to the CH$_3$-groups (H3) can be seen. The asymmetrical cross peaks are explained by the different polarization of the methyl and the methylene protons. The hyperpolarized geminal protons generate this cross peak (H1/2→H3), whereas the non-hyperpolarized methyl group may generate a cross peak (H3→H2/1), but the intensity is lower than the noise level and so not visible.

![Diagram of carbene intermediates](image)

**Figure S-8.** Aliphatic region of the $^1$H-OPSY-COSY spectrum confirming the coupling between the observed signals and the coupling to neighbored CH$_3$-groups.
Exchange Spectroscopy. The analysis of the OPSY-EXSY spectrum of the reaction 4b to 5b finds exchange correlations from the hyperpolarized hydrogens of the carbene 6c to a number of products and by-products, namely 5b, 10, 11 and free H₂, as shown in Figure 4 of the main text of the publication. These results are in excellent accord with the pathways 1 and 2 as proposed in Scheme 3. These observed exchange correlations are depicted by red arrows in Scheme S1. Interestingly, pathway 1 correctly predicts that only one of the olefinic hydrogens originates from the carbene 6c.
Scheme S1: Comparison of the exchange correlations (red arrows) extracted from the OPSY-EXSY from the carbene 6b. Greyed species are not observed by NMR. Hydrogens are colored to help follow their fate.

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