Mechanistic Investigations on Hydrogenation, Isomerization and Hydrosilylation Reactions Mediated by a Germyl-Rhodium System

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Supporting Information

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General considerations

All manipulations were carried out using standard Schlenk and glove-box techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. N-pentane (C₅H₁₂) was distilled under nitrogen over sodium. [D₆]Benzene was distilled under argon over sodium/benzophenone. Compounds [(ArMes₂)₂Ge:] (ArMes = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂), [RhCl(COD)]₂ (COD = 1,5-ciclooctadinene) and NaBAr₆ were prepared as described previously. Compounds 2 and 3 were recently reported by our group. Other chemicals were commercially available and used as received. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe₄ (δ: 0 ppm) using the residual proton solvent peaks as internal standards (¹H NMR experiments), or the characteristic resonances of the solvent nuclei (¹³C NMR experiments), while ³¹P was referenced to H₃PO₄. Spectral assignments were made by routine one- and two-dimensional NMR experiments (¹H, ¹³C{¹H}, ³¹P{¹H}, COSY, NOESY, HSQC and HMBC) where appropriate. Spectroscopic NMR resonances due to BAr⁺ anion: ¹H: δ 8.37 (s, 8H, o-Ar) and 7.67 (s, 4H, p-Ar) and ¹³C: 162.3 (q, ¹JCB = 50 Hz, ipso-Ar), 135.1 (s, o-Ar) and 117.7 (s, p-Ar).
Kinetic Analysis

H₂(and D₂)-semihydrogenation of diphenylacetylene catalyzed from 2.

*General Method*

In the glovebox, the appropriate mass of [(ArMes₂)₂ClGeRh] (1) was added as a solid to a J-Young NMR tube. Next, 0.1 mL of a freshly prepared stock-solution of hexamethylbenzene (S₁, 0.298 mM) in toluene-d₈ was added and the total volume was adjusted to 0.4 mL by subsequent addition of an appropriate volume of toluene-d₅. Afterward, an excess of NaBArF (20 mg) was added as a solid. The tube was sealed with a Teflon screw-cap to ensure air tightness and was vigorously shaken before being allowed to stand overnight at room-temperature. The formation of the catalyst 2 was monitored by ¹H NMR. After total conversion, 0.1 mL of a freshly prepared stock-solution of diphenylacetylene (S₂, 0.298 mM) in toluene-d₈ was added (Vₜot = 0.5 mL). Then, the NMR tube was degassed using freeze-pump method prior being charged at room temperature with hydrogen or deuterium (0.5 to 1.5 bar). Finally, the J-Young tube was placed in an oil bath at 80°C (NB: no reaction occurs at room-temperature). The extent of the reaction was monitored by ¹H NMR using relative integrations of diphenylacetylene (δ 7.47-7.41 ppm, m, 4H, Hₚh), catalyst (δ 7.66 ppm, br.s, 4H, Hₚ-Fxyl), cis-stilbene (δ 6.43 ppm, s, 2H, H₃₋₅₋₆₋₇₋₈₋₉₋₁₀₋₁₁_H), trans-stilbene (δ 7.33 ppm, ps.d, ¹JHH= 7.6 Hz, 4H, Hₚh) and diphenylethane (δ 2.71 ppm, s, 4H, H₃₋₅₋₆₋₇₋₈₋₉₋₁₀₋₁₁_H) regarding the integration of the methyl protons of hexamethylbenzene (δ 2.10, s, 18H, Hₘ₆) used here as an internal standard.
**Table S1. Reaction conditions for Exp 1-7.**

**H₂-trans-semihydrogenation**

**Experiment 1:**

| Reagents                  | Exp 1  | Exp 2  | Exp 3  | Exp 4  | Exp 5  | Exp 6  | Exp 7  |
|---------------------------|--------|--------|--------|--------|--------|--------|--------|
| Catalyst                  | 2,5 mg | 5,0 mg | 2,5 mg | 2,5 mg | 2,5 mg | 2,5 mg | 5,0 mg |
|                           | 0,00298 mmol | 0,00596 mmol | 0,00298 mmol | 0,00298 mmol | 0,00298 mmol | 0,00298 mmol | 0,00596 mmol |
| Hexamethylbenzene         | 0,1 mL of S₁ | 0,1 mL of S₁ | 0,1 mL of S₁ | 0,1 mL of S₁ | 0,1 mL of S₁ | 0,1 mL of S₁ | 0,1 mL of S₁ |
|                           | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol |
|                           | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. |
| NaBAr⁺                    | 20 mg  | 20 mg  | 20 mg  | 20 mg  | 20 mg  | 20 mg  | 20 mg  |
|                           | 0,0226 mmol | 0,0226 mmol | 0,0226 mmol | 0,0226 mmol | 0,0226 mmol | 0,0226 mmol | 0,0226 mmol |
|                           | 0,76 equiv. | 0,76 equiv. | 0,76 equiv. | 0,76 equiv. | 0,76 equiv. | 0,76 equiv. | 0,76 equiv. |
| Diphenylacetylene         | 0,1 mL of S₂ | 0,1 mL of S₂ | 0,1 mL of S₂ | 0,1 mL of S₂ | 0,1 mL of S₂ | 0,1 mL of S₂ | 0,1 mL of S₂ |
|                           | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol | 0,0298 mmol |
|                           | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. | 1 equiv. |
| H₂ or D₂                  | 1 bar  | 1 bar  | 1 bar  | 0,5 bar | 1,5 bar | 1 bar  | 1 bar  |
|                           | H₂     | H₂     | H₂     | H₂     | H₂     | D₂     | D₂     |
|                           | excess | excess | excess | excess | excess | excess | excess |

![Figure S1. ¹H NMR stacked spectra (tol-d₈, 300.13 MHz, 298 K) showing the extent of Exp 1.](image-url)
Figure S2. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 1; aromatic area.

Figure S3. Extent of Exp 1; evolution of the concentrations for each reagent and product over time as determined by $^1$H NMR.
Experiment 2:

Figure S4. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 2.

Figure S5. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 2; aromatic area.
**Figure S6.** Extent of Exp 2; evolution of the concentrations for each reagent and product over time as determined by $^1$H NMR.

**Experiment 3:**

**Figure S7.** $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 3.
Figure S8. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 3; aromatic area.

Figure S9. Extent of Exp 3; evolution of the concentrations for each reagent and product over time as determined by $^1$H NMR.
Experiment 4:

Figure S10. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 4.

Figure S11. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 4; aromatic area.
Figure S12. Extent of Exp 4; evolution of the concentrations for each reagent and product over time as determined by $^1$H NMR.

Experiment 5:

Figure S13. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 5.
Figure S14. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 5; aromatic area.

Figure S15. Extent of Exp 5; evolution of the concentrations for each reagent and product over time as determined by $^1$H NMR.
**Variable Time Normalization Analysis (VTNA)**

**Determination of the partial orders in catalyst and diphenylacetylene**

The Variable Time Normalization Analysis for the catalyst (cf. Figure S16) shows two profiles corresponding to Exp 1 (depicted in blue) and Exp 2 (depicted in red) and whose shape changes with the partial order simulated. A multipoint comparison clearly shows decent overlays for an order of 1 (a=1).

**Figure S16.** Variable Time Normalization Analysis for the determination the partial order in catalyst with another set of data.
The Variable Time Normalization Analysis for the diphenylacetylene (cf. Figure S17) shows two profiles corresponding to Exp 1 (depicted in blue) and Exp 3 (depicted in green) and whose shape changes with the partial order simulated. A multipoint comparison shows here also a good overlay for a zero order (b=0).

**Figure S17.** Variable Time Normalization Analysis for the determination the partial order in diphenylacetylene.
Initial rates analysis:

Determination of the partial order in hydrogen

The initial rates for Exp 1 (pH$_2$ = 1 bar), Exp 4 (pH$_2$ = 0.5 bar) and Exp 5 (pH$_2$ = 1.5 bar) can be extracted from diphenylacetylene’s consumption (see Figure S18). The initial concentrations of H$_2$ were determined from Henry’s law, $K_H = p_{H_2}/[H_2]$, where Henry’s law constant ($K_H$) for H$_2$ in toluene is 24.89 MPa L/mol. The plotting of ln($v_0$)=f(ln[H$_2$]) (see Figure S19) lead to a straight line with a slope of 0.95 corresponding to the partial order in hydrogen.

![Initial Rates](image)

**Figure S18.** Initial rates for consumption of diphenylacetylene in Exp 1, Exp 4 and Exp 5.

![Plot of ln($v_0$) as a function of ln[H$_2$]](image)

**Figure S19.** Plot of ln($v_0$) as a function of ln[H$_2$].
Determination of the observed rate constant for the cis-semihydrogenation of diphenylacetylene

According to the previous studies, the rate law of the *cis*-semihydrogenation of diphenylacetylene catalyzed from 2 can be written as such: \( v = k_{obs}[\text{cat}]^1[\text{dpa}]^0[H_2]^1 \). The observed rate constant \( k_{obs} \) was determined from the initial rates calculated in Exp 1, Exp 4 and Exp 5 according to the following equation:

\[
k_{obs} = \frac{v_0}{[H_2]_0^{1}[\text{cat}]_0^{1}} \quad \text{with} \quad [\text{cat}]_0 = [\text{cat}] = 0.00596 \text{ M}
\]

Thus, the rate constant could be estimated at:

\[
k_{obs} = 15.82 \pm 1.05 \text{ mol}^{-1} \text{L.min}^{-1} = 0.2637 \pm 0.0176 \text{ mol}^{-1} \text{L s}^{-1}
\]
**D₂-trans-semihydrogenation**

**Experiment 6:**

Figure S20. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 6.

Figure S21. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 6; aromatic area.
Experiment 7:

Figure S22. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 7.

Figure S23. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 7; aromatic area
Isotopic Studies:

To the overall transformation can be assigned the following kinetic law

\[ v = k_{obs}[dpa]^a pH_2^b [cat]^c \]

with \( k_{obs} \) the rate constant, \([dpa]\) the concentration in diphenylacetylene, \( pH_2 \) the pressure in hydrogen or deuterium, \([cat]\) the concentration in catalyst as well as \( a \), \( b \) and \( c \) their respective partial orders.

According to the initial rate method, the former equation can be noted for \textbf{Exp 1} and \textbf{Exp 2} as

\[ v_{0H} = k_H[dpa]_0^a pH_{20}^b [cat]^c. \]

Similarly, \textbf{Exp 6} and \textbf{Exp 7} verify the following equation

\[ v_{0D} = k_D[dpa]_0^a pH_{20}^b [cat]^c. \]

Since \textbf{Exp 1} and \textbf{Exp 6} were launched in the same conditions, then the ratio of their initial rates allows to determine the kinetic isotope effect (KIE) as stated by the following equation:

\[ \frac{v_{0H}}{v_{0D}} = \frac{k_H[dpa]_0^a pH_{20}^b [cat]^c}{k_D[dpa]_0^a pD_{20}^b [cat]^c} = \frac{k_H}{k_D} = KIE \]

This relation also applies to the comparative study of the initial rates for \textbf{Exp 2} and \textbf{Exp 7}.

**Figure S24.** Conversion of diphenylacetylene over time as determined by \(^1\text{H} \) NMR monitoring in \textbf{Exp 1} (depicted in bleu) and \textbf{Exp 6} (depicted in red). The initial rates for both reactions were respectively extracted from the linear functions connecting the two first measurements (depicted as solid dots).
Figure S25. Conversion of diphenylacetylene over time as determined by $^1$H NMR monitoring in Exp 2 (depicted in bleu) and Exp 7 (depicted in red). The initial rates for both reactions were respectively extracted from the linear functions connecting the two first measurements (depicted as solid dots).

The numerical applications of the former equations lead to the following results:

$$KIE = 3,52 \pm 0,26$$
H₂-semihydrogenation of diphenylacetylene catalyzed by 3 (isolated and generated in situ).

**Modus Operandi for catalysis by 3 generated in situ:**

A J-Young NMR tube was charged with \([(\text{Ar}^{\text{Mes}})_2\text{ClGeRh}] (1) (2.5 \text{ mg, 0.003 mmol, 10 mol%}).\] Hexamethylbenzene was introduced by addition of 0.1 mL of a freshly prepared stock-solution \((S_1, 0.298 \text{ mM})\) in toluene-\(d_8\). The total volume of the solution was adjusted to 0.4 mL by consecutive addition of 0.3 mL of toluene-\(d_8\). Afterward, NaBARf \((20 \text{ mg, 0.0226 mmol})\) was added at room-temperature, the tube was sealed with a Teflon screw-cap and the reaction was allowed to reach 80°C. After 6.5 hours at this temperature, \(^1\text{H} NMR monitoring showed total conversion of 2 into 3. Then, 0.1 mL of a freshly prepared stock-solution (0.298 mM) of diphenylacetylene (corresponding to 0.0298 mmol, 1 equiv.) was added. The solution was degassed by freeze-pump technic and charged at room-temperature with H₂ (1 bar). Finally, the solution was heated up to 80°C and the extent of the reaction was monitored by \(^1\text{H} NMR.

**Modus Operandi for catalysis from isolated 3:**

The reaction was launched in the same conditions than **Exp 1.** In the glovebox, \([(\text{Ar}^{\text{Mes}})_2\text{GeRhH}]\cdot\text{BARf} (3) (5.4 \text{ mg, 3.22.10}^{-6} \text{ mol, 0.10 equiv.) was added as a solid to a J-Young NMR tube. Next, 0.1 mL of a freshly prepared stock-solution of hexamethylbenzene \((S_1, 0.298 \text{ mM})\) in toluene-\(d_8\) was added and the total volume was adjusted to 0.43 mL by subsequent addition of an appropriate volume of toluene-\(d_8\). Then 0.11 mL (1 equiv.) of a freshly prepared stock-solution of diphenylacetylene \((S_2, 0.298 \text{ mM})\) in toluene-\(d_8\) was added \((V_{tot} = 0.54 \text{ mL, [3]}=0.00596 \text{ M})\). Then, the NMR tube was degassed using freeze-pump method prior being charged at room temperature with 1 bar of hydrogen. Finally, the solution was heated up to 80°C and the extent of the reaction was monitored by \(^1\text{H} NMR.
Comparison of the activities of catalyst 2 generated in situ and catalyst 3 generated in situ and isolated.

Figure S26. Comparison of the extents of the H$_2$-trans-semihydrogenations catalyzed from 2 generated in situ (Exp 1, solid triangles) and by 3 generated in situ (solid dots) and by isolated 3 (circles): Evolution of the concentration of diphenylacetylene (blue plots), cis-Stilbene (red plots), trans-Stilbene (green plots) and diphenylethane (grey plots).
H₂-semihydrogenation of diphenylacetylene catalyzed by 4.

The reaction was launched in the same conditions than Exp 1. In the glovebox, [(ArMes₂)₂GeRh].BArF (4) (4.7 mg, 2.83 \times 10^{-6} \text{ mol}, 0.10 equiv.) was added as a solid to a J-Young NMR tube. Next, 0.1 mL of a freshly prepared stock-solution of hexamethylbenzene (S₁, 0.298 mM) in toluene-d₈ was added and the total volume was adjusted to 0.385 mL by subsequent addition of an appropriate volume of toluene-d₈. Then 0.095 mL (1 equiv.) of a freshly prepared stock-solution of diphenylacetylene (S₂, 0.298 mM) in toluene-d₈ was added (V₂ = 0.48 mL, [4]=0.00596 M). Then, the NMR tube was degassed using freeze-pump method prior being charged at room temperature with 1 bar of hydrogen. Finally, the solution was heated up to 80°C and the extent of the reaction was monitored by ¹H NMR.

Figure S27. Comparison of the extents of the H₂-trans-semihydrogenations catalyzed from isolated 3 (circles) and from isolated 4 (solid dots): Evolution of the concentration of diphenylacetylene (blue plots), cis-Stilbene (red plots), trans-Stilbene (green plots) and diphenylethane (grey plots).
Trans-isomerization of cis-Stilbene catalyzed from 2.

**General Method**

In the glovebox, the appropriate mass of \([\text{Ar}^{\text{Mes}}]_2\text{ClGeRh} (1)\) was added as a solid to a J-Young NMR tube. Next, 0.1 mL of a freshly prepared stock-solution of hexamethylbenzene (\(S_1\), 0.298 mM) in toluene-\(d_8\) was added and the total volume was adjusted to 0.4 mL by subsequent addition of an appropriate volume of toluene-\(d_8\). Afterward, an excess of NaBAr\(^\text{F}\) was added as a solid. The tube was sealed with a Teflon screw-cap to ensure air tightness and was vigorously shaken before being allowed to stand overnight at room-temperature. The formation of 2 was monitored by \(^1\text{H} NMR. After total conversion, 0.1 mL of a freshly prepared stock-solution of cis-Stilbene (\(S_3\) for Exp 8 and 10, 0.298 mM; \(S_4\) for Exp 9, 0.894 mM) was added (\(V_{\text{int}} = 0.5 \text{ mL}\)). Then, the extent of the trans-isomerization was monitored over time by \(^1\text{H} NMR using relative integrations of the catalyst (\(\delta 7.66 \text{ ppm, br.s, 4H, H}_p\_\text{Fxyl}), \text{cis-stilbene (}\delta 6.43 \text{ ppm, s, 2H, H}_{\text{C=C}}), \text{trans-stilbene (}\delta 7.33 \text{ ppm, ps.d, } ^1J_{\text{HH}}= 7.6 \text{ Hz, 4H, H}_p\)) regarding the integration of the methylic protons of hexamethylbenzene (\(\delta 2.10, \text{s, 18H, H}_{\text{Me}}\)), used here as an internal standard.

![Catalyst diagram](image)

**Table S2.** Reaction conditions for Exp 8-10.
Trans-isomerization of cis-Stilbene

Experiment 8:

Figure S28. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 8.

Figure S29. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 8; aromatic area.
Figure S30. Extent of Exp 8: evolution of each reagent and product concentrations over time as determined by $^1$H NMR.

Experiment 9:

Figure S31. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 9.
Figure S32. $^1$H NMR stacked spectra (tol-\textit{d}_8, 300.13 MHz, 298 K) showing the extent of Exp 9; aromatic area.

**Exp 9**

**Figure S33.** Extent of Exp 9: evolution of each reagent and product concentrations over time as determined by $^1$H NMR.
Experiment 10:

Figure S34. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 10.

Figure S35. $^1$H NMR stacked spectra (tol-$d_8$, 300.13 MHz, 298 K) showing the extent of Exp 10; aromatic area.
Reaction Progress Kinetic Analysis (RPKA)

To the trans-isomerization of cis-Stilbene can be assigned the following kinetic law

\[ v = k [\text{cat}]^a [\text{cis} - \text{Stilbene}]^b \]

with k the rate constant, [cat] the concentration in catalyst, [cis-Stilbene] the concentration in cis-Stilbene and a and b their respective partial orders.

Since the concentration of the catalyst over the reaction time can be considered as constant, the latter equation can be simplified as

\[ v = k_{\text{obs}} [\text{cis} - \text{Stilbene}]^b \]

with \( k_{\text{obs}} \) the observed rate constant.

As such, the partial order b in cis-Stilbene can be theoretically determined by simple integrations of the kinetic law at different orders (0, 1, 2, …). However, in this peculiar case, the linear regressions of the different modelizations are too similar to clearly conclude by RPKA (e.g. Figure S37 to S39). This is why the kinetic resolution of the trans-isomerization was performed by Variable Time Normalization Analysis (VTNA).
Figure S37. Representative plots of [cis-Stilbene] over time and 0 order kinetic modeling for Exp 9.

Figure S38. Representative plots of ln[cis-Stilbene] over time and 1st order kinetic modeling Exp 9.

Figure S39. Representative plots of 1/[cis-Stilbene] over time and 2nd order kinetic modeling Exp 9.
**Variable Time Normalization Analysis (VTNA)**

**Determination of the partial orders in catalyst and cis-Stilbene:**

The Variable Time Normalization Analysis for the catalyst (cf. **Figure S40**) shows two profiles corresponding to Exp 8 (depicted in blue) and Exp 10 (depicted in red) and whose shape changes with the partial order simulated. A multipoint comparison clearly shows a decent overlay for an order of 1 (best fit for a broken order of 1.2).

![Figure S40](image)

**Figure S40. Variable Time Normalization Analysis** for the determination of the partial order in catalyst.

The Variable Time Normalization Analysis for the cis-Stilbene (cf. **Figure S41**) shows two profiles corresponding to Exp 8 (depicted in blue) and Exp 9 (depicted in green) and whose shape changes with the partial order simulated. A multipoint comparison shows here also a decent overlay for an order of 1 (best fit for a broken order of 0.8).

![Figure S41](image)

**Figure S41 Variable Time Normalization Analysis** for the determination of the partial order in cis-Stilbene.
The Normalization of the time scale in catalyst and in cis-Stilbene leads to an overlay of all reaction profiles in a straight confirming partial orders of 1,2 and 0,8 in catalyst and cis-Stilbene respectively (cf. Figure S42).

**Normalization of the time scale in catalyst and cis-Stilbene**

![Diagram](image)

\[ y = 1.5857x \]

\[ R^2 = 0.7978 \]

**Figure S42.** Normalization of the time scale in catalyst and in cis-Stilbene.

**Determination of the rate constant:**

The kinetic law can be approximated to

\[ v = k[cat]^1[cis - Stilbene]^1. \]

Since [cat] is constant over time (cf. Exp 8-10 above), the rate law can be written as such:

\[ v = k_{obs}[cis - Stilbene]^1 \]

with \( k_{obs} = k[cat]^1 \) and \([cat] = [cat]_0 = 0.00596 \text{ M}. \)

Then

\[ \frac{d[cis - Stilbene]}{[cis - Stilbene]^1} = k_{obs}dt \]

and \( k_{obs} \) can be determined from the plotting of

\[ ln[cis - Stilbene] = k_{obs}t + ln[cis - Stilbene]_0. \]

To do so, the mean value was calculated from **Exp 8** (repeated twice) and **Exp 9** (cf. Figure S43).
Figure S43. Plot of ln[cis-Stilbene] over time as determined by $^1$H NMR.

The linear regressions afford $k = 0.233 \pm 0.001 \text{ L.mol}^{-1}.\text{min}^{-1} = 3.88 \times 10^{-3} \pm 0.02 \times 10^{-3} \text{ L.mol}^{-1}.\text{s}^{-1}$.

**Isotopic Studies**

**Trans-isomerization of cis-Stilbene-d$_2$:**

In a J-Young NMR tube were added a 0.6 mL solution of benzene-d$_6$ containing diphenylacetylene (5.31 mg, 0.0298 mmol), hexamethylbenzene (5.2 mg, 0.0320 mmol) and the Lindlar’s catalyst (1.6 mg, 0.0298 mmol). Then, the NMR tube was charged with deuterium gas (1.5 bar) after the solution was degassed at the Schlenk line using freeze-pump method. Finally, the J-Young tube was placed in an oil bath at 80°C for 2.5 hours leading to the formation of a mixture of diphenylacetylene (3%), cis-Stilbene (63%) and trans-Stilbene (7%) as determined by the $^1$H NMR relative integrations of each species regarding hexamethylbenzene. Next, the solution was degassed and filtered. Afterward,
[(ArMes)2ClGeRh] (1) (1.47 mg, 0.00175 mmol) was added followed by addition of NaBARF (20 mg) and the total volume of the solution was adjusted to 0.85 mL by addition of supplementary benzene-d6. After an overnight standing at room temperature, 1H NMR monitoring showed the formation of 2 (0.0027 M) and a concentration in cis-Stilbene-d2 of 0.0222 M. The tube was then allowed to reach 100°C and the extent of the trans-isomerization was here also monitored by 1H NMR.

**Figure S44.** Plot of ln[cis-Stilbene-d2] over time as determined by 1H NMR.

The integration of the kinetic law corresponding to partial orders of 1 in cis-Stilbene-d2 and in catalyst lead to a rate constant k = 0.170 L.mol⁻¹.min⁻¹ = 2.838·10⁻³ L.mol⁻¹.s⁻¹ (cf. Figure S44).

**Trans-isomerization of cis-Stilbene:**

For the sake of comparison, the isomerization of cis-Stilbene has been launched in approximated same conditions than in the isomerization of cis-Stilbene-d2. In a J-Young NMR tube was prepared a 0.9 mL solution containing cis-Stilbene (0.1 mL from a stock solution in benzene-d6 at 0.175 mM, 0.0175 mmol, 1 equiv.), hexamethylbenzene (5.0 mg, 0.031 mmol), [(ArMes)2ClGeRh] (1) (1.47 mg, 0.00175 mmol, 10 mol%) and NaBARF (20 mg). The solution was let stand overnight at room-temperature prior being heated to 100°C. The extent of the trans-isomerization was here also monitored by 1H NMR.

**Figure S45.** Plot of ln[cis-Stilbene] over time as determined by 1H NMR.
The integration of the kinetic law corresponding to partial orders of 1 in cis-Stilbene and in catalyst lead to a rate constant \( k = 1.214 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1} = 2.023 \times 10^{-5} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) (cf. Figure S47).

**Kinetic Isotope Effect:**

From Figure S44 and S45 could be determined \( k_0 = 0.170 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1} = 2.838 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) and \( k_H = 1.214 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1} = 2.023 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \) respectively, leading to a *Kinetic Isotope Effect* of:

\[
\frac{k_H}{k_0} = KIE = 7.12
\]

**Activation parameters for the insertion of cis-Stilbene in the Rh-H bond of compound 3.**

The trans-isomerization reaction was repeated three times in the same conditions than for Exp 8 but at different temperature: 80°C, 90°C and 100°C. Here again, the plotting of ln[cis-Stilbene] over time lead to the extraction of the rate constant at the different temperatures. The results are gathered in Table S3 below:

| T (°C) | k (L.mol\(^{-1}\).s\(^{-1}\)) |
|-------|-------------------------------|
| 80    | 0.00607                       |
| 90    | 0.01662                       |
| 100   | 0.02957                       |

**Table S3.** Rate constants of trans-isomerization of cis-Stilbene at 80°C, 90°C and 100°C.

From the previous data can be calculated the Eyring parameters (cf. Table S4):

| T (K)  | k (L.mol\(^{-1}\).s\(^{-1}\)) | ln(k/T) | 1/T   |
|--------|-------------------------------|----------|-------|
| 353,4  | 0.006065012                   | -10,9728194 | 0,00282965 |
| 365,3  | 0.016617963                   | -9,99799 | 0,00273748 |
| 372,8  | 0.02956539                    | -9,44219294 | 0,0026824 |

**Table S4.** Calculated coordinates for the Eyring plot.

The Eyring equation states the following relationship between k and \( \Delta G^\circ \):

\[
\ln \left( \frac{k}{T} \right) = -\frac{\Delta G^\circ}{RT} + \ln \left( k \frac{k_b}{h} \right)
\]

Then we end-up with the following equation:

\[
\ln \left( \frac{k}{T} \right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln \left( k \frac{k_b}{h} \right)
\]

The experimental plot of the Eyring equation leads to the following linear law with a very good fit (cf. Figure S46):

\[
\ln \left( \frac{k}{T} \right) = A \times \frac{1}{T} + B
\]
Where

\[ A = - \frac{\Delta H^\neq}{R} \]
\[ B = \frac{\Delta S^\neq}{R} + \ln(\kappa \frac{k_b}{h}) \]

With

\( \Delta H^\neq = \) activation enthalpy
\( \Delta S^\neq = \) activation entropy

\( k_b = \) Boltzmann constant = 1.38064852 × 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^2 \cdot \text{K}^{-1} 
\( h = \) Planck constant = 6.62607004 × 10^{-34} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-1} 
\( \kappa = \) transmission coefficient = 1 = the probability that an activated complex forms a particular set of products rather than reverting to reactants or forming alternative product (often taken as unity in monomolecular reaction) 
\( R = \) ideal gas constant = 1.9858775 × 10^{-3} \text{ kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} 
\( A = -1.04133 \times 10^4 \) 
\( B = 18.50 \)

**Eyring Plot**

\[ y = -1.04133E+04x + 1.84972E+01 \]
\[ R^2 = 9.99849E-01 \]

**Figure S46.** Representative Eyring plot of the insertion of *cis*-Stilbene in the Rh-H bond.

Therefore, the kinetic activation parameters of the reaction are:

\( \Delta H^\neq = 20.67948 \pm 0.50823 \text{ kcal.mol}^{-1} \) and \( \Delta S^\neq = -0.01045 \pm 0.00140 \text{ kcal.K}^{-1} \cdot \text{mol}^{-1} \)
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