SUPPORTING INFORMATION FOR

Does the rate of competing isomerisation during alkene metathesis depend on pre-catalyst initiation rate?

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General Experimental

Kinetic data were acquired using a Bruker Avance II spectrometer (600 MHz ¹H observe frequency), equipped with TBI-α probe (inverse ¹H/¹³C/BB) and temperature control. All kinetic experiments were acquired at 298 K, with an interpulse delay of 35 s to ensure accurate quantification; relaxation times for signals corresponding to many components in the reaction mixtures are known to be up to ca. 7 s.¹ Data were processed using Bruker Topspin (version 2.1 or 3.0) and Microsoft Excel (2007 or 2010).

Complexes G1, G2 and GH2 were purchased from Sigma Aldrich and used as supplied. Zhan1B and Grela2 were purchased from Strem. M823-SIPr was supplied by Omega Cat System (Rennes, France). Benzene-d₆, chloroform-d and toluene-d₈ were purchased from Sigma Aldrich, and dichloromethane-d₂ was purchased from Goss Scientific. Deuterated solvents were dried on activated 4 Å molecular sieves overnight and degassed with a stream of nitrogen or argon, unless otherwise stated. 1,8-Nonadiene was purchased from Sigma Aldrich and passed through a pad of activated alumina before use.
Kinetic Data Plots

1,8-nonadiene **3 mol% G1**  benzene-$d_6$  (*Figure 1*)

\[ y = 2.78 \times 10^{-4}x - 4.54 \times 10^0 \]

\[ R^2 = 9.94 \times 10^{-1} \]
1,8-nonadiene 3 mol% G2 benzene-$d_6$ (Figure 2)
1,8-nonadiene  3 mol% GH2  benzene-$d_6$  (Figure 3)
1,8-nonadiene  3 mol% Zhan1B benzene-\(d_6\) (Figure 3)
1,8-nonadiene  3 mol% Grela2  benzene-\text{d}_6  \text{(Figure 3)}

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1,8-nonadiene  3 mol% $\text{M}_{\text{SIPr}}$  benzene-$d_6$  (Figure 4)
1,8-nonadiene 3 mol% G2 chloroform-d (Figure 5)
1,8-nonadiene  3 mol% G2  undried chloroform-d

Concentration / mM

Time / s

Cyclohexene  Cyclic Dimer  Cycloheptene

Concentration / mM

Time / s

Alkylidene  Methylidene  Pre-Catalyst

Electronic Supplementary Material (ESI) for Dalton Transactions
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1,8-nonadiene  3 mol% G2  DCM-$d_2$  (Figure 5)

- Cyclohexene
- Cyclic Dimer
- Cycloheptene

- Pre-Catalyst
- Alkylidene
- Ethylidene
- Methylidene

Concentration /mM vs. Time /s graph.
1,8-nonadiene 3 mol% G2 toluene-$d_8$ (Figure 5)

![Graph 1](image1.png)

![Graph 2](image2.png)

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Cycloheptene 3 mol% G2 benzene-$d_{6}$ (Figure 6)

Concentration / mmol L$^{-1}$

Time / s

Concentration / mM

Time / s
Electronic Supplementary Material (ESI) for Dalton Transactions
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Initiation Rate Measurement for Zhan1B

The initiation rate for this complex was determined by monitoring the reaction of the pre-catalyst with ethyl vinyl ether in DCM solution at 298 K using UV/visible spectroscopy, using the same apparatus and method used for the determination of the initiation rate constants for complexes GH$_2^2$ and Grela$_2^3$.

\[
\text{[ethyl vinyl ether] / mol L}^{-1} \quad k_{\text{obs}} / \text{s}^{-1} \\
0.02676 \quad 0.00336 \\
0.02662 \quad 0.00379 \\
0.05055 \quad 0.00695 \\
0.05029 \quad 0.00705 \\
0.10320 \quad 0.01409 \\
0.10267 \quad 0.01405 \\
0.20205 \quad 0.02626 \\
0.20101 \quad 0.02624
\]

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{rate_constant_graph.png}
\caption{Graph of rate constant $k_{\text{obs}}$ vs. [ethyl vinyl ether] / mol L$^{-1}$}
\end{figure}

References