Supporting Information

for

Mixed N-Heterocyclic Carbene/Phosphite Ruthenium Complexes: Towards a New Generation of Olefin Metathesis Catalysts

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1 General Information

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. \(^1\)H, \(^13\)C-{\(^1\)H} and \(^31\)P-{\(^1\)H} 1D and 2D Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 Ultrashield spectrometer using the residual solvent peak as reference (CHCl\(_3\): \(\delta_{\text{H}} = 7.26\) ppm, \(\delta_{\text{C}} = 77.16\) ppm; CH\(_2\)Cl\(_2\), \(\delta_{\text{H}} = 5.32\) ppm, \(\delta_{\text{C}} = 53.80\) ppm.) at 298K. Variable temperature NMR spectra were carried out in CD\(_3\)NO\(_2\).

2 Procedures for catalysis

Substrates 2, \(^4\) 4, \(^6\) 6, \(^8\) 8\(^i\) and 11\(^1\) were synthesised according to literature procedures. NMR spectra of the RCM products 3, \(^1\) 5, \(^5\) 7, \(^7\) 10, \(^12\) 12, \(^13\) 13, \(^8\) 14, \(^14\) 14, \(^15\) 15, and \(^16\) 16\(^2\) were compared to previously reported analyses.

2.1 Procedure for Table 1 – Comparison trans/cis-Caz-1

A flame-dried schlenk was charged with a solution of the substrate (0.25 mmol) in 2.5 mL of solvent (0.1M, CH\(_2\)Cl\(_2\) for room temperature experiments and toluene for 80°C) and Caz-1 (1 to 2 mol%) was added. The reaction mixture was stirred at the appropriate temperature for the appropriate amount of time. The solvent was removed in vacuo. The conversion was determined by \(^1\)H NMR (CDCl\(_3\)).

2.2 Procedure for Figure 4 – Comparison of catalysts

A reaction tube (Radleys carousel 12 reaction station) was charged with a solution of di(methallyl)tosylamine 11 (0.5 mmol) in toluene (0.5 mL) and the ruthenium pre-catalyst (0.5 mol%) was added. The reaction mixture was stirred at 80°C and aliquots were taken every 5 to 20 minutes. Each aliquot was then added to a solution of 40 µL of ethylvinyl ether and toluene. All samples were then subjected to GC analysis to determine the conversion of 11 to 12.

2.3 Solvent optimisation

In order to test the reactivity limits of the phosphite system and to demonstrate its true potential, low catalyst loading experiments were conducted on RCM reactions using a less challenging substrate, namely 2. As cis-Caz-1 is efficient and stable at elevated temperature, several solvents with high boiling points were tested in the model RCM of 2. All reactions were conducted at reflux in the presence of 0.01 mol% of cis-Caz-1 (Table 1). Solvents with lower boiling point (ca. 80°C) and water gave poor conversions to 3 (entries 1-3). On the other hand, aromatic solvents proved highly beneficial to the system as they all lead to high conversion to the RCM product, independently of the reaction temperature (Table 1, entries 4-
Finally, unusual solvents for RCM such as hexanol, dimethylacetamide (DMA) and ethylene glycol were evaluated and gave low conversions (Table 1, entries 7-10). Interestingly, DMA, which is known as a catalyst poison, surprisingly allowed for 20% of the cyclised product, which corresponds to a turnover number of 2 000.

### Table S1 Solvent optimisation at low catalyst loading

<table>
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<tr>
<th>Entry</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Conv. (%)</th>
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<td>1,2-dichloroethane</td>
<td>80</td>
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<td>2</td>
<td>dimethoxyethane</td>
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<tr>
<td>5</td>
<td>chlorobenzene</td>
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<tr>
<td>8</td>
<td>dimethylacetamide</td>
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<td>9</td>
<td>1,2-dichlorobenzene</td>
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<tr>
<td>10</td>
<td>ethylene glycol</td>
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<td>2</td>
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Reaction conditions: 2 (0.25 mmol), cis-Caz-1 (0.01 mol%), solvent (0.5 mL), reflux, 20h. Conversions were determined by $^1$H NMR based on diene.

### Procedure

A reaction tube (Radleys carousel 12 reaction station) was charged with a solution of the substrate (0.25 mmol) in 2.5 mL of solvent and cis-Caz-1 (0.01 mol% from stock solution). The reaction mixture was stirred at reflux temperature for 20 hours. The solvent was removed in vacuo. The conversion was determined by $^1$H NMR (CDCl$_3$).

#### 2.4 Procedure for Scheme 2 - Catalytic RCM at low catalyst loading

In the glovebox, a vial was charged with a stirring bar, substrate (0.25 mmol), pre-catalyst cis-Caz-1 (from a stock solution of 2.2 mg in 2 mL of toluene), and 0.5 mL of toluene. The mixture was stirred outside the glovebox at the indicated temperature. After 20h, the reaction was stopped and solvent was evaporated. Flash chromatography (pentane/diethylether - 9:1 to 8:2 v:v) on silica gel afforded the title compounds.
3 Synthesis and characterisation of pre-catalysts Caz-1

3.1 Trans-Caz-1

Triisopropylphosphite (296 µL, 1.3 mmol) was added to a solution of Ind-III (1 g, 1.3 mmol) in CH₂Cl₂ (15 mL). The reaction mixture was stirred at room temperature for 30 min. The solvent was concentrated in vacuo to 1 mL and pentane (10 mL) was added. The solution was filtered and the solvent was removed in vacuo, leading to a microcrystalline red solid. Trans-Caz-1 was obtained in 76% yield as a mixture of trans and cis isomers 9:1 (866 mg).

$^1$H NMR on mixture trans/cis 9:1 (CD₂Cl₂, 400 MHz): $\delta$ (ppm) = 0.88 (d, $^3J_{HH} = 6.1$ Hz, 9H, CH-CH₃), 0.91 (d, $^3J_{HH} = 6.1$ Hz, 9H, CH-CH₂), 1.80 (s, 3H, mesityl CH₃), 1.97 (s, 3H, mesityl CH₃), 2.25 (s, 3H, mesityl CH₃), 2.33 (s, 3H, mesityl CH₃), 2.69 (s, 3H, mesityl CH₃), 2.73 (s, 3H, mesityl CH₃), 3.75-3.91 (m, 2H, carbene H⁴ and CH-CH₂), 6.08 (s, 1H, mesityl CH), 6.18 (s, 1H, mesityl CH), 6.44 (s, 1H, mesityl CH), 6.86 (s, 1H, indenylidene H¹), 6.99 (s, 1H, indenylidene H⁴), 7.01 (s, 2H, mesityl CH), 7.15 (ddd, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 1.0$ Hz, 1H, indenylidene H⁵), 7.24 (ddd, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 1.1$ Hz, 1H, indenylidene H⁵), 7.39-7.42 (m, 2H, indenylidene H¹⁰), 7.51-7.55 (m, 1H, indenylidene H¹¹), 7.70-7.73 (m, 2H, indenylidene H⁹), 8.32 (dd, $^3J_{HH} = 7.4$ Hz, $^3J_{HH} = 0.8$ Hz, 1H, indenylidene H⁷).

$^{13}$C-$^1$H NMR on mixture trans/cis 9:1 (CDCl₃, 100.6 MHz) $\delta$ (ppm) = 18.67 (s, mesityl CH₃), 18.73 (s, mesityl CH₃), 20.43 (s, mesityl CH₃), 20.45 (s, mesityl CH₃), 21.0 (s, mesityl CH₃), 21.2 (s, mesityl CH₃), 23.8 (s, CH-CH₃), 23.88 (s, CH-CH₃), 23.92 (s, CH-CH₃), 52.4 (d, $^4J_{CP} = 8.9$ Hz, carbene C⁴), 52.45 (d, $^4J_{CP} = 11.2$ Hz, carbene C⁵), 69.9 (d, $^2J_{CP} = 3.5$ Hz, CH-CH₃), 116.5 (s, indenylidene C⁶), 126.8 (s, indenylidene C¹¹), 128.2 (s, indenylidene C⁵), 128.7 (s, indenylidene C⁶), 129.2 (s, indenylidene C¹⁰), 129.37 (s, mesityl CH), 129.41 (s, mesityl CH), 129.79 (s, indenylidene C¹), 129.81 (s, mesityl CH), 135.7 (s, C⁴), 136.6 (s, C⁴), 136.7 (s, C⁴), 136.78 (s, C⁴), 136.81 (s, C⁴), 137.0 (s, C⁴), 137.4 (s, C⁴), 138.3 (s, indenylidene C⁵), 138.6 (s, C⁴), 139.6 (s, C⁴), 141.0 (s, C⁴), 141.6 (s, C⁴), 143.5 (d, $^3J_{CP} = 1.9$ Hz, indenylidene C⁷), 217.3 (d, $^2J_{CP} = 127.8$ Hz, carbene C⁵), 301.7 (d, $^2J_{CP} = 21.0$ Hz, indenylidene C¹).

$^{31}$P-$^1$H NMR on mixture trans/cis 9:1 (CD₂Cl₂, 162 MHz) $\delta$ (ppm) = 113.8.

Elem. anal.: Calcd. for C₄₅H₅₇Cl₂N₂O₃PRu: C, 61.64; H, 6.55; N, 3.19. Found: C, 61.45; H, 6.34; N, 3.35.
3.2 Cis-Caz-1:

Under an inert atmosphere, trisopropylphosphite (60 µL, 0.26 mmol) was added to a solution of Ind-III (196 mg, 0.26 mmol) in dichloromethane (4 mL). The mixture was stirred for 15h at 40°C, allowed to cool to room temperature, and concentrated in vacuo to 1 mL. Pentane (10 mL) was added and the precipitate was collected by filtration and washed with pentane (3 x 5 mL). Cis-Caz-1 was obtained as a brown solid in 85% yield (193 mg, 0.22 mmol).

1H NMR (CD2Cl2, 400 MHz): δ (ppm) = 0.58 (d, 3JHH = 5.9 Hz, 3H, CH-CH3), 0.75 (d, 3JHH = 6.0 Hz, 3H, CH-CH3), 0.92 (d, 3JHH = 5.8 Hz, 3H, CH-CH3), 1.06 (d, 3JHH = 6.0 Hz, 3H, CH-CH3), 1.43 (d, 3JHH = 6.1 Hz, 3H, CH-CH3), 1.48 (d, 3JHH = 6.2 Hz, 3H, CH-CH3), 1.58 (s, 3H, mesityl CH3), 1.85 (s, 3H, mesityl CH3), 2.33 (s, 3H, mesityl CH3), 2.56 (s, 3H, mesityl CH3), 2.64 (s, 3H, mesityl CH3), 2.73 (s, 3H, mesityl CH3), 3.23 (m, 1H, CH-CH3), 3.58-3.67 (m, 1H, carbene H1), 3.76-3.91 (m, 3H, carbene H3, H5), 4.30 (m, 1H, CH-CH3), 4.82 (m, 1H, CH-CH3), 6.13 (s, 1H, mesityl CH), 6.45 (s, 1H, indenylidene H2), 6.48 (s, mesityl CH), 7.00 (s, 2H, mesityl CH), 7.14 (d, 3JHH = 7.2 Hz, 1H, indenylidene H8), 7.30-7.36 (m, 2H, indenylidene H3 and H9), 7.38-7.42 (m, 2H, indenylidene H10), 7.46-7.50 (m, 1H, indenylidene H11), 7.69 (d, 3JHH = 7.2 Hz, 2H, indenylidene H7), 8.87 (d, 3JHH = 7.1 Hz, 1H, indenylidene H1).

13C-{1H} NMR (CDCl3, 100.6 MHz) δ (ppm) = 19.1 (s, mesityl CH3), 19.5 (s, mesityl CH3), 20.6 (s, mesityl CH3), 21.1 (s, mesityl CH3), 21.4 (s, mesityl CH3), 21.5 (s, mesityl CH3), 24.0 (s, CH-CH3), 24.05 (s, CH-CH3), 24.3 (s, CH-CH3), 24.4 (s, CH-CH3), 24.72 (s, CH-CH3), 24.74 (s, CH-CH3), 52.0 (s, carbene C4H), 52.6 (s, carbene C3H), 69.55 (d, 2JCP = 11.7 Hz, CH-CH3), 70.7 (d, 2JCP = 9.3 Hz, CH-CH3), 72.9 (d, 2JCP = 3.6 Hz, CH-CH3), 117.4 (s, indenylidene C4H), 127.6 (s, indenylidene C9H), 128.7 (s, indenylidene C11H), 129.2 (s, indenylidene C10H), 129.8 (s, indenylidene C4H), 129.9 (s, indenylidene C5H), 130.26 (s, mesityl CH), 130.31 (s, mesityl CH), 130.5 (s, mesityl CH and indenylidene C7H), 135.0 (s, CIV), 135.9 (s, CIV), 136.8 (s, CIV), 136.9 (s, CIV), 137.0 (s, CIV), 138.1 (s, CIV), 138.25 (s, CIV), 138.5 (s, CIV), 138.6 (s, CIV), 139.2 (s, CIV), 140.4 (d, 3JCP = 15.9 Hz, indenylidene C2), 141.2 (d, 3JCP = 2.6 Hz, indenylidene C7a), 142.5 (s, CIV), 208.95 (d, 2JCP = 13.4 Hz, carbene C2), 292.1 (d, 2JCP = 24.7 Hz, indenylidene C1).

31P-{1H} NMR (CD2Cl2, 162 MHz) δ (ppm) = 122.0.


Crystal data for cis-Caz-1: Crystals were obtained by slow diffusion (CH2Cl2/n-dodecane). C45H57Cl2N2O3PRu M = 876.87, monoclinic, space group P21/c, a = 19.132 (2) Å, b = 9.5576 (11) Å, c = 24.397 (3) Å, β = 104.451 (3)°, V = 4320.0 (9) Å3, Z = 4, ρcalcd = 1.348 g.cm−3, μ (Mo Kα) = 0.56 mm−1, T = 125 (2) K, Rint = 0.132, 7916 unique reflections, R1 = 0.0897, wR2 = 0.1676 for 5696 reflections with I > 2σ(I), R1 = 0.1341, wR2 = 0.1900 for all data, GOF = 1.197.
4 NMR spectra

4.1 $^1$H NMR (CD$_2$Cl$_2$) of trans-Caz-1 (contains 10% of cis-Caz-1)

4.2 $^{13}$C-$^1$H NMR (CD$_2$Cl$_2$) of trans-Caz-1 (contains 10% of cis-Caz-1)
4.3 $^{31}$P-$^1$H NMR (CD$_2$Cl$_2$) of trans-Caz-1 (contains 10% of cis-Caz-1)
4.4 $^1$H NMR (CD$_2$Cl$_2$) of cis-Caz-1

4.5 $^{13}$C-{$^1$H} NMR (CD$_2$Cl$_2$) of cis-Caz-1
4.6 $^{31}$P-$^1$H NMR (CD$_2$Cl$_2$) of cis-Caz-1
trans-Caz-1
mixture trans/cis-Caz-1 9:1

cis-Caz-1
4.7 $^1$H NMR (CDCl$_3$) of 3

4.8 $^1$H NMR (CDCl$_3$) of 5
4.9 $^1$H NMR (CDCl$_3$) of 7

4.10 $^1$H NMR (CDCl$_3$) of 10
4.11 $^1$H NMR (CDCl$_3$) of 12

4.12 $^1$H NMR (CDCl$_3$) of 13
4.13 $^1$H NMR (CDCl$_3$) of 14

![NMR spectrum of 14]

4.14 $^1$H NMR (CDCl$_3$) of 15

![NMR spectrum of 15]
4.15 $^1$H NMR (CDCl$_3$) of 16
5 NMR Kinetic studies, Eyring plot

Procedure for the kinetic plots:
In a glovebox, a J-Young tube was charged with ca. 4 mg of complex trans-1 (ca. 90% pure) and 0.6 mL of CD$_3$NO$_2$. $^1$H NMR spectra were recorded on a Varian Unity Plus-500 MHz spectrometer every 20 minutes at the appropriate temperature. 5 experiments were conducted at 30°C, 40°C, 50°C and 60°C and an additional at 40°C in the presence of 5 equiv of P(OiPr)$_3$. Results are plotted in Fig. 1. Data for this plot are reported at the end of this section in Table 3.

Equations leading to the Eyring plot:
As the observed kinetics in Fig. 1 seem to be first order, the following equations were used. The decrease in concentration of trans-Caz-1 (indicated as trans-1 in this section) over time can be written as equation (1):

$$ V = -\frac{d[\text{trans-1}]}{dt} = k.[\text{trans-1}] \quad (1) $$

Equation (2) represents the differential form of the rate law. Integration of (2) gives (3):

$$ \ln[\text{trans-1}] = -k.t + C \quad (3) $$

C represents the constant of integration and is obtained when $t = 0$ and $[\text{trans-1}] = [\text{trans-1}]_0$.

$$ C = \ln([\text{trans-1}]_0) \quad (4) $$

Finally, integrating equation (4) in equation (3) gives (5):

$$ \ln\left[\frac{[\text{trans-1}]}{[\text{trans-1}]_0}\right] = -k.t \quad (5) $$

Fig. 1 Isomerisation of complex 1 in CD$_3$NO$_2$. 

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Plots of equation (5) at the 4 different temperatures studied are represented in Fig. 2. As straight lines are obtained, the first assumption that reaction was first order is confirmed. The slopes of these straight lines gave kinetic constants k (see Table 2).

![Fig. 2 Plots of \[\ln\left(\frac{\text{trans-1}}{\text{trans-1}_0}\right)\] against time (in seconds) at temperature from 30°C to 60°C.]

### Table 2 Kinetic constant values

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<thead>
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<th>Temperature (°C)</th>
<th>k (s⁻¹)</th>
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<tr>
<td>30</td>
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<tr>
<td>40</td>
<td>0.0001197</td>
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<td>50</td>
<td>0.0003778</td>
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<tr>
<td>60</td>
<td>0.0011587</td>
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</table>

The general form of the Eyring-Polanyi equation is the following:

\[
k = k_b \frac{T}{h} e^{-\frac{\Delta G^\neq}{RT}} (6)
\]

Where: \( \Delta G^\neq \) is the Gibbs energy of activation,
\( k_b \) is the Boltzmann’s constant \((1.38 \times 10^{-23} \text{ J.K}^{-1})\),
\( h \) is Planck’s constant \((6.63 \times 10^{-34} \text{ J.s})\),
\( R \) is the gas constant \((8.32 \text{ J.K}^{-1}.\text{mol}^{-1})\) and
\( T \) is the absolute temperature (in K).

Knowing that \( \Delta G^\neq = \Delta H^\neq - T.\Delta S^\neq \), linearising equation (6) gives (7):

\[
\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^\neq}{RT} + \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\neq}{R} (7)
\]

Plot of \(\ln(k/T)\) against \(1/T\), or in our case \(1000/T\), gives the Eyring plot (Fig. 3).

The slope of straight line gives:

\[
\frac{\Delta H^\neq}{R} = 11395 \text{ K}
\]

and the intercept:

\[
\ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\neq}{R} = 21.63
\]
Finally, after conversions, the enthalpy of activation is $\Delta H^{\neq} = 22.6 \text{ kcal.mol}^{-1}$ and the entropy is $\Delta S^{\neq} = -4.2 \text{ cal.mol}^{-1}.\text{K}^{-1}$.

**Fig. 3.** Eyring plot of the trans/cis isomerisation of 1.
**Table 3** Kinetic data for Fig. 1

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<tr>
<th>30°C Time (s)</th>
<th>40°C [trans-1]/[trans-1]₀</th>
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6 References