

*Electronic Supplementary Information for*

**Transfer hydrogenation with abnormal dicarbene rhodium(III) complexes  
containing ancillary and modular imine ligands**

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**Variable Temperature NMR Studies and the Calculation of the Free Energy of Inversion.** The CD<sub>3</sub>CN solutions of the complex were cooled to –20 °C using a 500 MHz NMR machine and the low temperature <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were then recorded. The sample was then heated in 10 °C intervals while recording of the <sup>1</sup>H NMR spectrum at each interval was likewise carried out. The coalescence temperature (T<sub>c</sub>) for the NCH<sub>2</sub>N and the *i*Pr methyl signals were estimated for each complex **2a–d** and are shown in Tables S1 and S2. From the T<sub>c</sub> for each complex, the free energy of inversion (ΔG) of the imidazolylidene linker (NCH<sub>2</sub>N) and the *i*Pr methyl groups were estimated using equation 1. The main source of error was in the estimation of the T<sub>c</sub> for which the ΔG value for each calculation is derived. The overlay of variable temperature <sup>1</sup>H NMR spectra showing the slow exchange limit and the coalescence of the NCH<sub>2</sub>N <sup>1</sup>H NMR signals with increased temperature is shown in Figure S1.

**Table S1.** <sup>1</sup>H NMR data, coalescence temperature and free energy estimation based on the coalescence temperature of the NCH<sub>2</sub>N linker <sup>1</sup>H NMR signals (CD<sub>3</sub>CN solutions).

Complex	δ <sub>H</sub> (ppm)/ J <sub>HH</sub> (Hz)	T <sub>c</sub> (°C)	δv (Hz)	ΔG (kJ/mol)
<b>2a</b>	6.99 (13.1), 6.15 (13.1)	60	420	63±1
<b>2b</b>	6.97 (13.1), 6.15 (13.1)	55 <sup>a</sup>	410	62±1
<b>2c</b>	6.96 (13.1), 6.14 (13.1)	50	410	61±1
<b>2d</b>	6.94 (13.2), 6.16 (13.2)	50	390	61±1

<sup>a</sup> The coalescence for complex **2b** occurred between 50 and 60 °C and was estimated at 55 °C.

**Table S2.**  $^1\text{H}$  NMR data, coalescence temperature and free energy estimation based on the coalescence temperature of the *i*Pr methyl group  $^1\text{H}$  NMR signals.

Complex	$\delta_{\text{H}}$ (ppm)/ $J_{\text{HH}}$ (Hz)	$T_{\text{c}}$ ( $^{\circ}\text{C}$ )	$\delta\nu$ (Hz)	$\Delta\text{G}$ (kJ/mol)
<b>2a</b>	1.62 (6.6), 1.40 (6.6)	40	110	$63\pm 1$
<b>2b</b>	1.61 (6.6), 1.40 (6.6)	$35^{\text{a}}$	105	$62\pm 1$
<b>2c</b>	1.61 (6.6), 1.40 (6.6)	$35^{\text{a}}$	105	$62\pm 1$
<b>2d</b>	1.64 (6.6), 1.41 (6.6)	30	115	$60\pm 1$

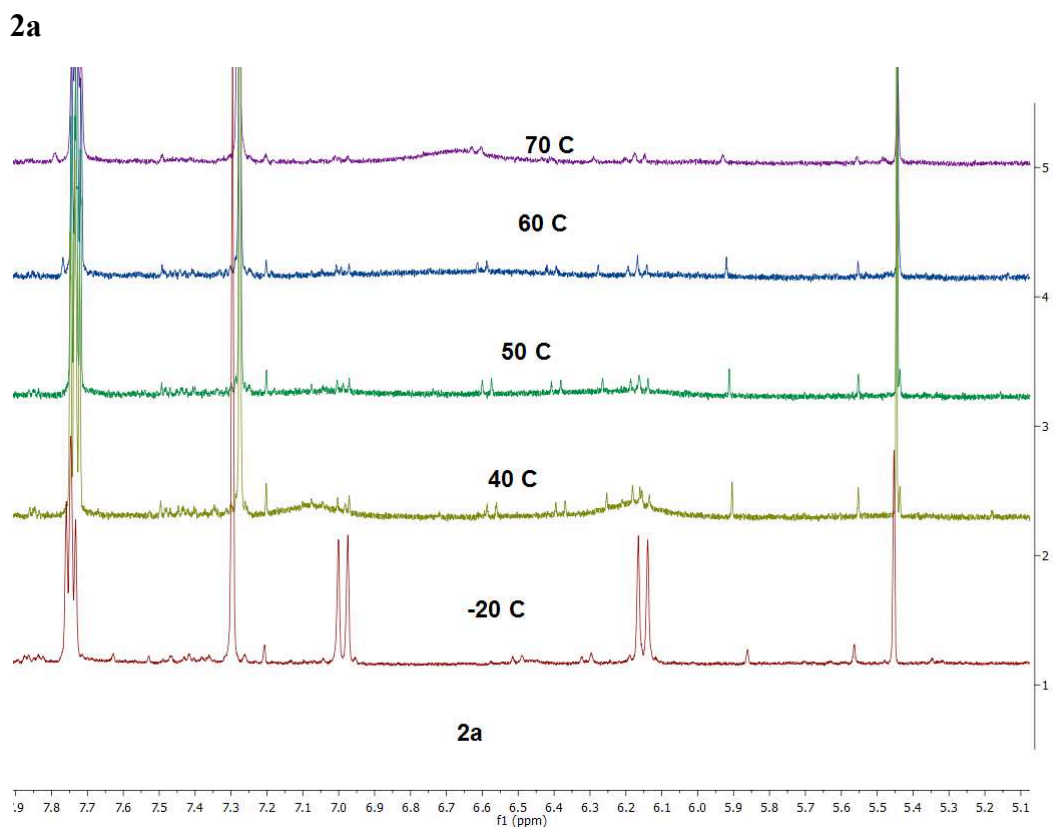
<sup>a</sup> The coalescence for the *i*Pr  $^1\text{H}$  NMR signals of complexes **2b** and **2c** occurred between 30 and 40  $^{\circ}\text{C}$  and were therefore estimated at 35  $^{\circ}\text{C}$ .

$$\Delta\text{G} = RT_{\text{c}}(22.96 + \ln(T_{\text{c}}/\delta\nu)) \quad (1)$$

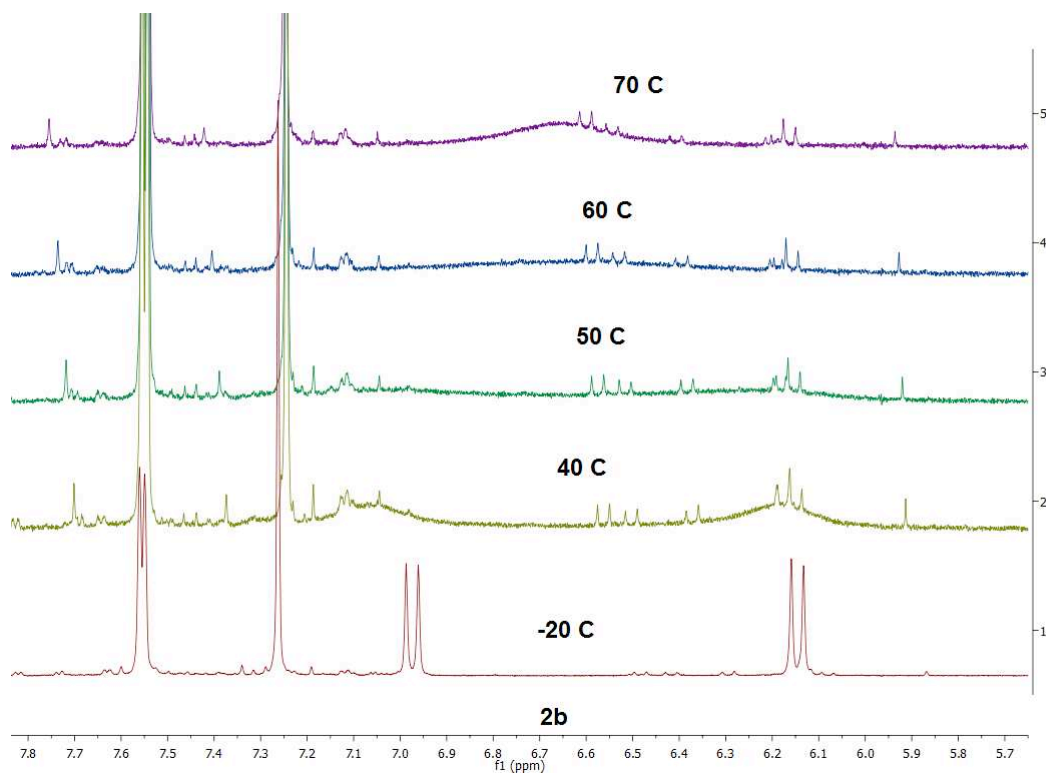
where  $R = 8.3144$  (for unit of J/mol)

$T_{\text{c}}$  = coalescence temperature (in K)

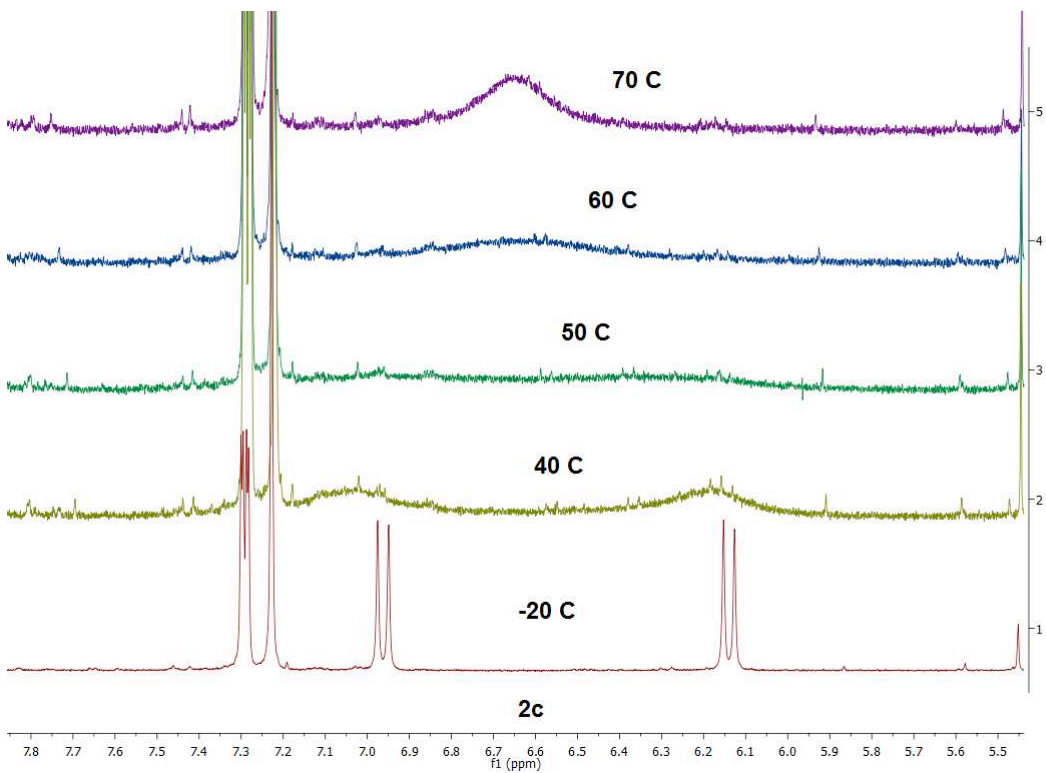
$\delta\nu$  = difference between  $^1\text{H}$  NMR signals at slow-exchange limit (in Hz)

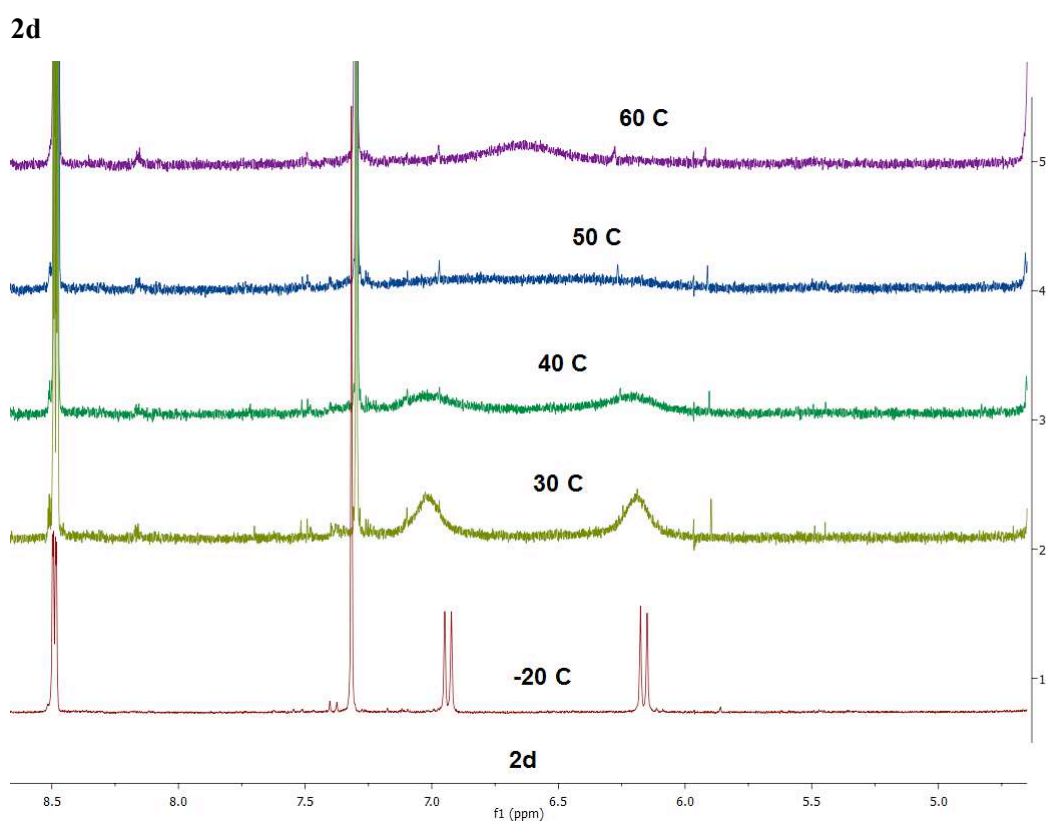


**2b**



**2c**





**Figure S1.** Variable temperature  $^1\text{H}$  NMR spectra overlays showing the slow exchange limit ( $-20\text{ }^\circ\text{C}$ ) and the coalescence of the  $\text{NCH}_2\text{N}$  protons with heating for complexes **2a–d**.

**Table S3.** Crystal data and structure refinement for **2a** and **2b**.

	<b>2a</b>	<b>2b</b>
CCDC No.	1437163	1437165
Empirical formula	C <sub>27</sub> H <sub>35</sub> N <sub>7</sub> RhI <sub>3</sub>	C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> Cl <sub>2</sub> RhI <sub>3</sub>
Molecular formula	[C <sub>25</sub> H <sub>32</sub> N <sub>6</sub> RhI <sub>2</sub> ] <sup>+</sup> [I] <sup>-</sup> • C <sub>2</sub> H <sub>3</sub> N	[C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> Cl <sub>2</sub> RhI <sub>2</sub> ] <sup>+</sup> [I] <sup>-</sup> • CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	941.23	1013.15
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca (#61)	P2 <sub>1</sub> /c (#14)
Unit cell dimensions	a= 18.4957(2) Å α= 90°. b= 18.0877(1) Å β= 90°. c= 19.1324(2) Å γ= 90°.	a= 11.0534(1) Å α= 90°. b= 33.3241(3) Å β= 108.238(1)°. c= 10.6127(1) Å γ= 90°.
Volume	6400.64(10) Å <sup>3</sup>	3712.75(6) Å <sup>3</sup>
Z	8	4
Density (calculated)	1.953 Mg/m <sup>3</sup>	1.813 Mg/m <sup>3</sup>
Absorption coefficient	3.456 mm <sup>-1</sup>	24.829 mm <sup>-1</sup>
F(000)	3600	1944
Crystal size (mm <sup>-3</sup> )	0.3092 × 0.1872 × 0.0570 mm <sup>3</sup>	0.1373 × 0.1207 × 0.0386 mm <sup>3</sup>
θ range	2.72 to 32.96°.	4.21 to 76.95°.
Index ranges	-23 ≤ h ≤ 28, -27 ≤ k ≤ 27, -28 ≤ l ≤ 26	-10 ≤ h ≤ 13, -41 ≤ k ≤ 41, -13 ≤ l ≤ 13
Reflections collected	74243	55077
Independent reflections	11370 [R(int) = 0.0259]	7742 [R(int) = 0.0510]
Completeness	(θ = 32.00°) 98.8 %	(θ = 76.95°) 98.9 %
Absorption correction	Analytical	Analytical
Max., min. transmission	0.888, 0.631	0.476, 0.156
Data	11370	7742
Restraints / parameters	0 / 355	6 / 369 <sup>a)</sup>
Goodness-of-fit on F <sup>2</sup>	1.127	1.058
Final R indices [I > 2σ(I)]	R1 = 0.0242, wR2 = 0.0530	R1 = 0.0420, wR2 = 0.1120
R indices (all data)	R1 = 0.0328, wR2 = 0.0581	R1 = 0.0452, wR2 = 0.1150
Largest diff. peak, hole	1.081, -1.704 e.Å <sup>-3</sup>	2.214, -1.285 e.Å <sup>-3</sup>

<sup>a)</sup> The two disorder parts were restrained to have the same shape using SADI.

**Table S4.** Crystal data and structure refinement for **4**

	<b>4</b>
CCDC No.	1437164
Empirical formula	C <sub>32</sub> H <sub>39</sub> N <sub>7</sub> Cl <sub>4</sub> RhI <sub>3</sub>
Molecular formula	[C <sub>30</sub> H <sub>35</sub> N <sub>7</sub> RhI] <sup>2+</sup> {[I] <sup>-</sup> } <sub>2</sub> • 2 (CH <sub>2</sub> Cl <sub>2</sub> ) <sup>a)</sup>
Formula weight	1147.11
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Triclinic
Space group	P-1 (#2)
Unit cell dimensions	a= 11.0304(3) Å α= 85.577(3)°. b= 13.3992(4) Å β= 78.000(3)°. c= 14.0098(4) Å γ= 80.837(3)°.
Volume	1997.46(10) Å <sup>3</sup>
Z	2
Density (calculated)	1.907 Mg/m <sup>3</sup>
Absorption coefficient	24.378 mm <sup>-1</sup>
F(000)	1104
Crystal size	0.2880 × 0.1335 × 0.0384 mm <sup>3</sup>
θ range	3.23 to 77.29°.
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	81077
Independent reflections	8346 [R(int) = 0.0748]
Completeness	(θ = 77.29°) 98.5 %
Absorption correction	Analytical
Max., min. transmission	0.466, 0.035
Data	8346
Restraints / parameters	0 / 386
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indices [I > 2σ(I)]	R1 = 0.0473, wR2 = 0.1282
R indices (all data)	R1 = 0.0491, wR2 = 0.1296
Largest diff. peak, hole	2.390, -1.543 e.Å <sup>-3</sup>

<sup>a)</sup> The solvent could not be modelled in terms of atomic sites. Platon SQUEEZE was used to compensate for the spread electron density.