Supporting Information for the paper

Activation of an unstrained C(sp^2)—C(sp^2) single bond using chelate-bisphosphinite Rh(I) complexes

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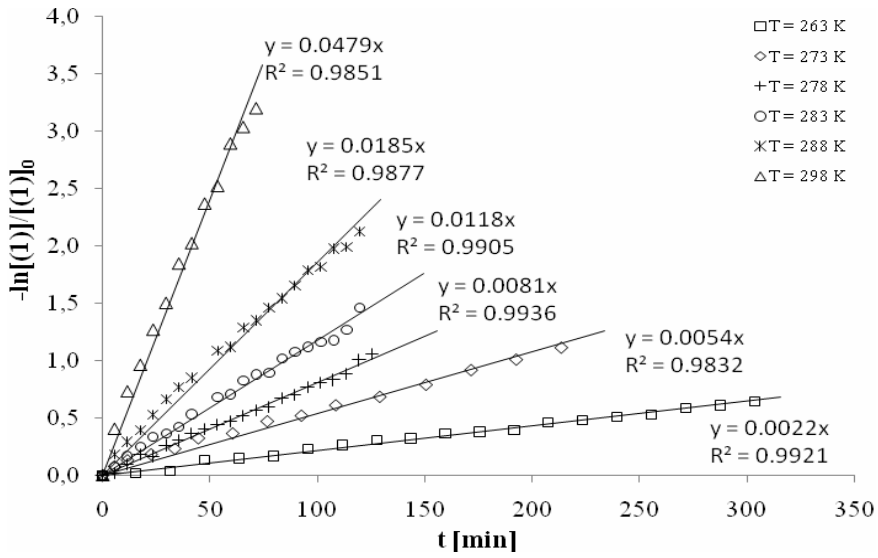
Kinetic evaluation for the formation of 2b



Evaluation of the $^{31}P\{^{1}H\}$ NMR signal integrals
assuming a first order rate law for the formation of **2b.**

T = 263K

t [min]	[(1)]/[(1)]$_0$	- ln [(1)]/[(1)]$_0$
0	1.0000	0.00
15.5	0.9804	0.02
31.5	0.9615	0.04
47.5	0.8772	0.13
63.5	0.8621	0.15
79.5	0.8475	0.17
95.5	0.7937	0.23
111.5	0.7692	0.26
127.5	0.7353	0.31
143.5	0.7246	0.32
159.5	0.6944	0.36
175.5	0.6849	0.38
191.5	0.6757	0.39
207.5	0.6329	0.46
223.5	0.6173	0.48
239.5	0.6024	0.51
255.5	0.5882	0.53
271.5	0.5556	0.59
287.5	0.5435	0.61
303.5	0.5263	0.64

T = 273K

t [min]	[(1)]/[(1)]$_0$	- ln [(1)]/[(1)]$_0$
0	1.0000	0.00
5.5	0.9259	0.08
11.5	0.8772	0.13
22.5	0.8333	0.18
33.5	0.7937	0.23
44.5	0.7246	0.32
60.5	0.6944	0.36
76.5	0.6250	0.47
92.5	0.5952	0.52
108.5	0.5435	0.61
129.0	0.5051	0.68
150.5	0.4545	0.79
171.5	0.4000	0.92
192.5	0.3650	1.01
213.5	0.3289	1.11

T = 278K

t [min]	[(1)]/[(1)]$_0$	- ln [(1)]/[(1)]$_0$
0	1.0000	0.00
5.5	0.9804	0.02
11.5	0.9091	0.10
17.5	0.8333	0.18
23.5	0.8475	0.17
29.5	0.7692	0.26
35.5	0.7353	0.31
41.5	0.6944	0.36
47.5	0.6667	0.41
53.5	0.6410	0.44
59.5	0.6250	0.47
65.5	0.5952	0.52
71.5	0.5682	0.57
77.5	0.5495	0.60
83.5	0.5102	0.67
89.5	0.4950	0.70
95.5	0.4630	0.77
101.5	0.4464	0.81
107.5	0.4348	0.83
113.5	0.4132	0.88
119.5	0.3650	1.01
125.5	0.3472	1.06

T = 283K

t [min]	$[(1)]/[(1)]_0$	$- \ln [(1)]/[(1)]_0$
0	1.0000	0.00
5.5	0.9259	0.08
11.5	0.8475	0.17
17.5	0.7813	0.25
23.5	0.7143	0.34
29.5	0.6944	0.36
35.5	0.6579	0.42
41.5	0.5882	0.53
53.5	0.5051	0.68
59.5	0.4950	0.70
65.5	0.4386	0.82
71.5	0.4167	0.88
77.5	0.4098	0.89
83.5	0.3623	1.02
89.5	0.3425	1.07
95.5	0.3268	1.12
101.5	0.3125	1.16
107.5	0.3086	1.18
113.5	0.2825	1.26
119.5	0.2331	1.46

T = 288K

t [min]	$[(1)]/[(1)]_0$	$- \ln [(1)]/[(1)]_0$
0	1.0000	0.00
5.5	0.8333	0.18
11.5	0.7463	0.29
17.5	0.6757	0.39
23.5	0.5882	0.53
29.5	0.5155	0.66
35.5	0.4630	0.77
41.5	0.4274	0.85
53.5	0.3378	1.09
59.5	0.3268	1.12
65.5	0.2762	1.29
71.5	0.2591	1.35
77.5	0.2315	1.46
83.5	0.2137	1.54
89.5	0.1916	1.65
95.5	0.1672	1.79
101.5	0.1623	1.82
107.5	0.1385	1.98
113.5	0.1370	1.99
119.5	0.1196	2.12

T = 298K

t [min]	$[(1)]/[(1)]_0$	$- \ln [(1)]/[(1)]_0$
0	1.0000	0.00
5.5	0.6667	0.41
11.5	0.4808	0.73
17.5	0.3817	0.96
23.5	0.2809	1.27
29.5	0.2222	1.50
35.5	0.1577	1.85
41.5	0.1319	2.03
47.5	0.0935	2.37
53.5	0.0801	2.52
59.5	0.0553	2.89
65.5	0.0479	3.04
71.5	0.0407	3.20
77.5	0.0402	3.21

In a screw cap NMR tube with a septum were placed 14.2 mg of $[Rh(coe)_2Cl]_2$ and 2 equiv. of L2 under argon. The sample was cooled with liquid nitrogen in a Dewar vessel and 0.5 ml of toluene was added with a syringe. After placing the probe in the NMR spectrometer at 193K the complete dissolution of the two compounds was waited for (until no free ligand was visible in the $^{31}P\ \{^1H\}$ NMR spectrum anymore). Next the desired temperature was chosen and at least 10 min waited for thermal equilibration (the VT-unit of the NMR machine was calibrated using a sample of 1,2 ethanediol according to Org. Magn. Reson. 12 (1979) 569). The reaction sample was placed in a Dewar vessel with liquid nitrogen in the mean time. In defined temperature-dependent time intervals $^{31}P\ \{^1H\}$ NMR spectra were taken and the integrals of the two observable species extracted. No reliable integration was possible below 263K due to increasing line broadening (Figure 1). Above 300 K the reaction became too fast for an accurate evaluation using $^{31}P\ \{^1H\}$ NMR. 0.04 mol/L $[Rh(coe)_2Cl]_2$ were used for all kinetic evaluations.

Table 1. Rate constants for the exchange in the Rh(I) complex **1** at variable temperatures.

T [K]	k [s^{-1}] x 10^{-3}
193	0.49(2)
203	0.83(7)
213	1.87(13)
218	3.47(20)
223	4.57(20)
233	26.0(5)
238	30.7(7)
243	45.0(8)
253	108(1)
263	286(1)
273	525(3)
283	956(10)
293	1996(43)
303	2937(87)

Table 2. equilibrium constants for the reaction **3a**$\rightarrow$**2a**

T [K]	**K_{eq}**
223	4.7
233	5.4
243	6.1
253	6.9
263	9.1
273	11.1
283	12.5
293	14.3
303	16.7