Electronic Supplementary Information for Dalton Transactions

Metal-free dihydrogen activation chemistry: structural and dynamic features of intramolecular P/B pairs

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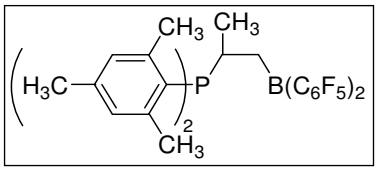
Dedicated to Professor Hans-Joachim Galla on the occasion of his 60th birthday

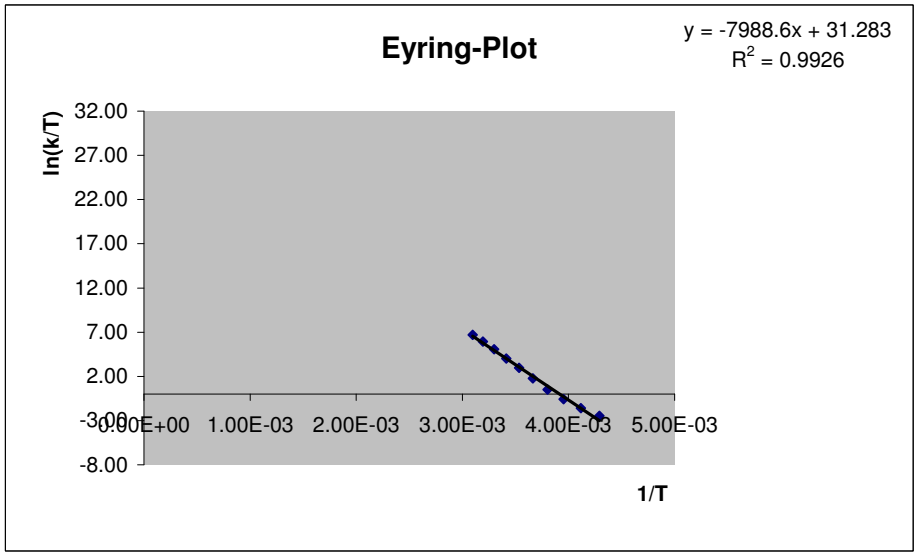
Supporting Information

lineshape analyse of **9a** (psp407) in toluene



T1/T2	T [K]	site 1		site 2		Int 1	Int 2	k(1,2) [s-1]	K = Int2/Int1	k(2,1) [s-1]	$G_{12}^{\#}$ [kJ/mol] with f_{Green}	$G_{21}^{\#}$ [kJ/mol] with f_{Green}	G^0 [kJ/mol]	1/T	ln(k(1,2)/T) with f_{Green}	ln(k(2,1)/T) with f_{Green}
0.5	333	450	-3467	-450	-3467	*0.500*	0.500	260000	1.000	260000	45.42	45.42	0.00	3.00E-03	7.35	7.35
0.5	323	450	-3467	-450	-3467	*0.500*	0.500	130000	1.000	130000	45.84	45.84	0.00	3.10E-03	6.69	6.69
0.5	313	450	-3467	-450	-3467	*0.500*	0.500	60000	1.000	60000	46.35	46.35	0.00	3.19E-03	5.95	5.95
0.5	303	450	-3467	-450	-3467	*0.500*	0.500	24000	1.000	24000	47.10	47.10	0.00	3.30E-03	5.07	5.07
0.5	293	450	-3467	-450	-3467	*0.500*	0.500	8000	1.000	8000	48.14	48.14	0.00	3.41E-03	4.00	4.00
0.5	283	450	-3467	-450	-3467	*0.500*	0.500	2800	1.000	2800	48.88	48.88	0.00	3.53E-03	2.99	2.99
0.5	273	450	-3467	-450	-3467	*0.500*	0.500	800	1.000	800	49.92	49.92	0.00	3.66E-03	1.77	1.77
0.5	263	450	-3467	-450	-3467	*0.500*	0.500	220	1.000	220	50.83	50.83	0.00	3.80E-03	0.51	0.51
0.5	253	450	-3467	-450	-3467	*0.500*	0.500	70	1.000	70	51.23	51.23	0.00	3.95E-03	-0.59	-0.59
0.5	243	450	-3467	-450	-3467	*0.500*	0.500	25	1.000	25	51.20	51.20	0.00	4.12E-03	-1.58	-1.58
0.5	233	450	-3467	-450	-3467	*0.500*	0.500	10	1.000	10	50.79	50.79	0.00	4.29E-03	-2.46	-2.46

Konstanten 8.31441 1.38E-23 4 184 6.63E-34



$k_{chem}(1,2) = f_{Green}(1,2) * k(1,2)$ $\quad k_{chem}(2,1) = f_{Green}(2,1) * k(2,1)$

$f_{Green}(1,2) =$ 2

$$\Delta G^{\neq} = RT * \left[23{,}76 - ln\left(\frac{k_{chem}}{T}\right) \right]$$

$$ln\left(\frac{k_{chem}}{T}\right) = -\frac{\Delta H^{\neq}}{R} * \frac{1}{T} + \left(23{,}76 + \frac{\Delta S^{\neq}}{R}\right)$$

slope -7988.6
axis-intercept 31.28

$$\Delta H^{\neq} = -R * slope$$

$$\Delta S^{\neq} = (axis - intercept - 23{,}76) * R$$

ΔG_{283K}	**48.9**	kJ/mol
$\Delta H^{\neq}$	**66.4**	kJ/mol
$\Delta S^{\neq}$	**62.5**	J/mol/K

with f_{Green} with f_{Green}

Fehlerfortpflanzungsgesetz		
s_G	$s_{\ln((k1,2)/T)}$	$s_{1/T}$
0.40054778	0.1001802	1.80E-05
0.4029939	0.10019152	1.92E-05
0.40690508	0.10020394	2.04E-05
0.41318744	0.10021761	2.18E-05
0.42251374	0.1002327	2.33E-05
0.43182771	0.10024941	2.50E-05
0.44462783	0.10026799	2.68E-05
0.45865436	0.10028873	2.89E-05
0.47113693	0.10031197	3.12E-05
0.48237132	0.10033813	3.39E-05
0.49227919	0.10036772	3.68E-05

$s_T = 2$

$s_k = 0.1*k$

law of propagation of error:

$$s_{f(x_1,x_2,\ldots x_i)} = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial f(x_i)}{\partial x_i}\right)^2 \cdot {s_{x_i}}^2}$$

Error calculation of kinetic parameters (law of error propagation)

Estimated standard deviation of temperature:

```
> st:=2;
```

$$st := 2$$

Estimated standard deviation of k:

```
> sk:=0.1*k;
```

$$sk := 0.1\,k$$

Green factor gf:

```
> gf:=2;
```

$$gf := 2$$

Error of ΔG, calculated by the "law of error propagation":

```
> g:=R*T*(23.76-ln(gf*k/T));
```

$$g := RT\left(23.76 - \ln\left(\frac{2\,k}{T}\right)\right)$$

```
> f1:=diff(g,T);
```

$$f1 := R\left(23.76 - \ln\left(\frac{2\,k}{T}\right)\right) + R$$

```
> f2:=diff(g,k);
```

$$f2 := -\frac{RT}{k}$$

```
> sg:=sqrt((f1^2)*(st^2)+(f2^2)*(sk^2));
```

$$sg := \sqrt{4\left(R\left(23.76 - \ln\left(\frac{2\,k}{T}\right)\right) + R\right)^2 + 0.01\,R^2\,T^2}$$

Error of ln(k/T), calculated by the "law of error propagation": :

```
> h:=ln(gf*k/T);
```

$$h := \ln\left(\frac{2\,k}{T}\right)$$

```
> f3:=diff(h,T);
```

$$f3 := -\frac{1}{T}$$

```
> f4:=diff(h,k);
```

$$f4 := \frac{1}{k}$$

```
> sh:=sqrt((f3^2)*(st^2)+(f4^2)*(sk^2));
```

$$sh := \sqrt{\frac{4}{T^2} + 0.01}$$

Error of 1/T, calculated by the "law of error propagation":

```
> i:=1/T;
```

$$i := \frac{1}{T}$$

```
> f5:=diff(i,T);
```

$$f5 := -\frac{1}{T^2}$$

```
> f6:=diff(i,k);
```

$$f6 := 0$$

```
> si:=sqrt((f5^2)*(st^2)+(f6^2)*(sk^2));
```

$$si := 2\sqrt{\frac{1}{T^4}}$$

```
>
```