Mechanistic studies on the formation of η^2-diphosphine (η^6-*p*-cymene)ruthenium(II) compounds

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SUPPLEMENTARY MATERIAL

1. Simulation analysis of the ^{31}P-NMR spectrum of [2c]PF_6

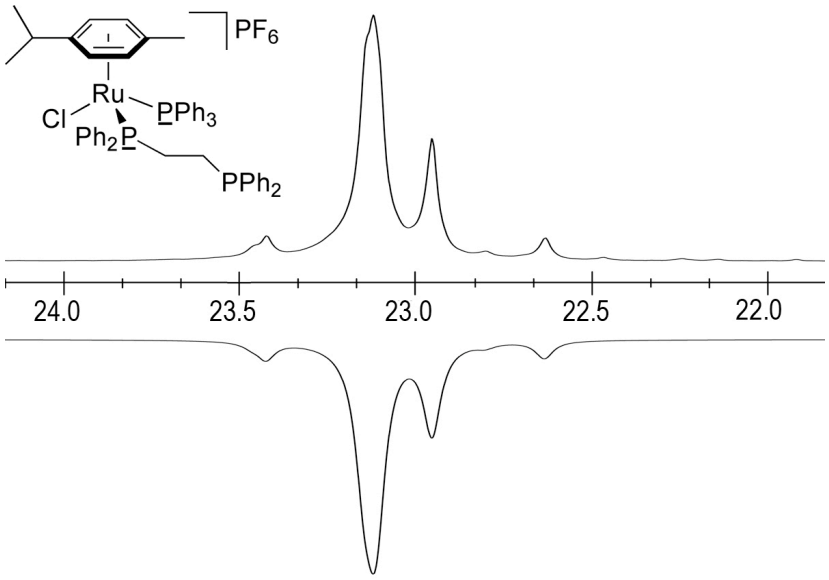

Figure S1: Observed (above) and simulated (below) ^{31}P-NMR spectrum of **[2c]PF_6**.

2. Solid state structures of $[2a]PF_6$ and $[2d]PF_6$

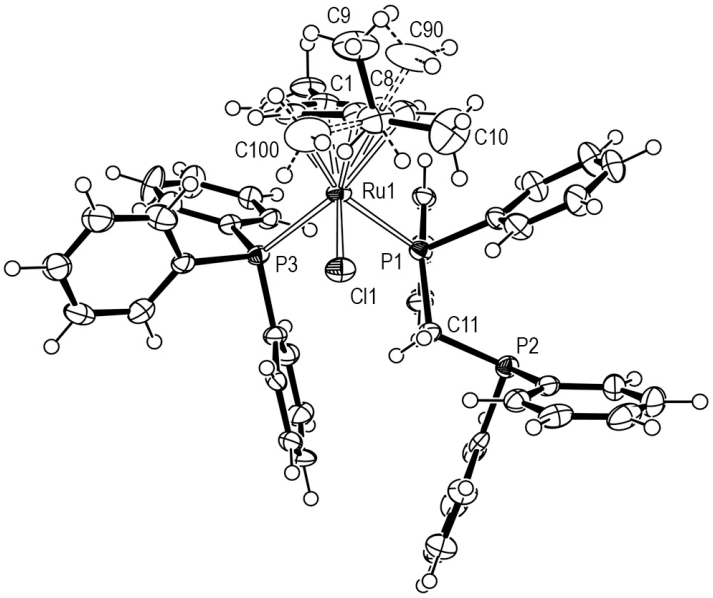

Figure S2: ORTEP representation of **$[2a]PF_6$** thermal ellipsoids are drawn at 50% probability level. Counter ion and solvent molecules omitted for clarity. The minor disordered component is shown with dashed bonds (C90 and C100). Relevant bond parameters are given in Table 2 (manuscript).

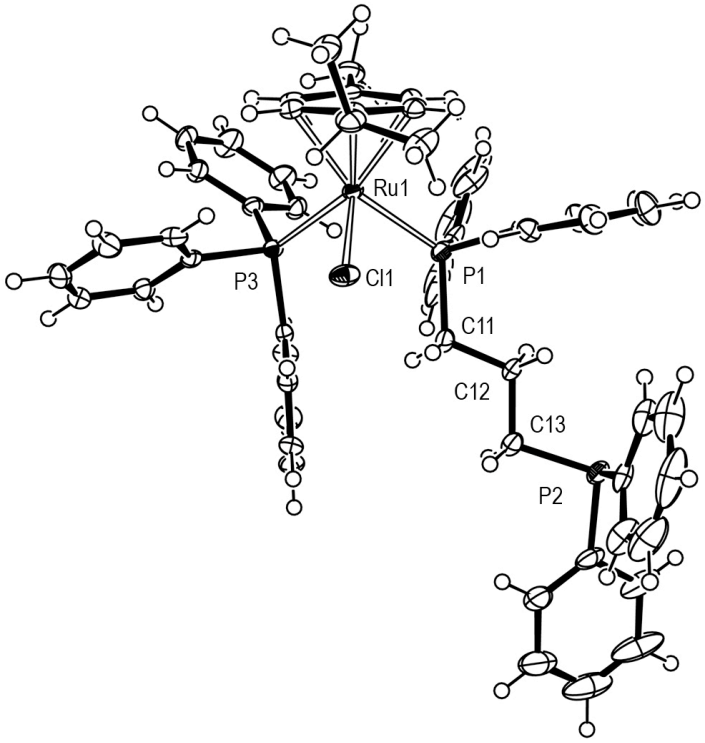

Figure S3: ORTEP representation of **$[2d]PF_6$**; thermal ellipsoids are drawn at 50% probability level. Counter ion and solvent molecules omitted for clarity. Relevant bond parameters are given in Table 2 (manuscript).

3. Kinetic studies of 4a and 4b

Table S1: Rate constants for chelation reactions of **4a** and **4b** at different temperatures.[a]

		ligand	solvent (v/v)	T / K	$10^4 \cdot k_{obs}$ / s^{-1}	R^2_{fit}
1	**4a→[5a]Cl**	dppm	1:1 MeOH-CH_2ClCH_2Cl	280.4	0.144 ± 0.006	0.998
2		dppm	1:1 MeOH-CH_2ClCH_2Cl	297.6	1.45 ± 0.08	0.997
3		dppm	1:1 MeOH-CH_2ClCH_2Cl	303.4	3.1 ± 0.2	0.994
4		dppm	1:1 MeOH-CH_2ClCH_2Cl	312.6	9.7 ± 1.3	0.987
5	**4b→[5b]Cl**	dppv	1:1 MeOH-CH_2ClCH_2Cl	265.2	0.113 ± 0.011	0.992
6		dppv	1:1 MeOH-CH_2ClCH_2Cl	281.9	0.90 ± 0.06	0.996
7		dppv	1:1 MeOH-CH_2ClCH_2Cl	297.6	6.4 ± 0.7	0.993
8		dppv	1:1 MeOH-CH_2ClCH_2Cl	303.4	11.4 ± 1.1	0.992
9		dppv	CH_2ClCH_2Cl	315.4	0.190 ± 0.014	0.999
10		dppv	CH_2ClCH_2Cl	326.2	0.69 ± 0.14	0.998
11		dppv	CH_2ClCH_2Cl	338.2	2.7 ± 0.2	0.997
12		dppv	CH_2ClCH_2Cl	349.2	7.2 ± 0.4	0.999

[a] Errors quoted are the standard errors calculated from the exponential fitting.

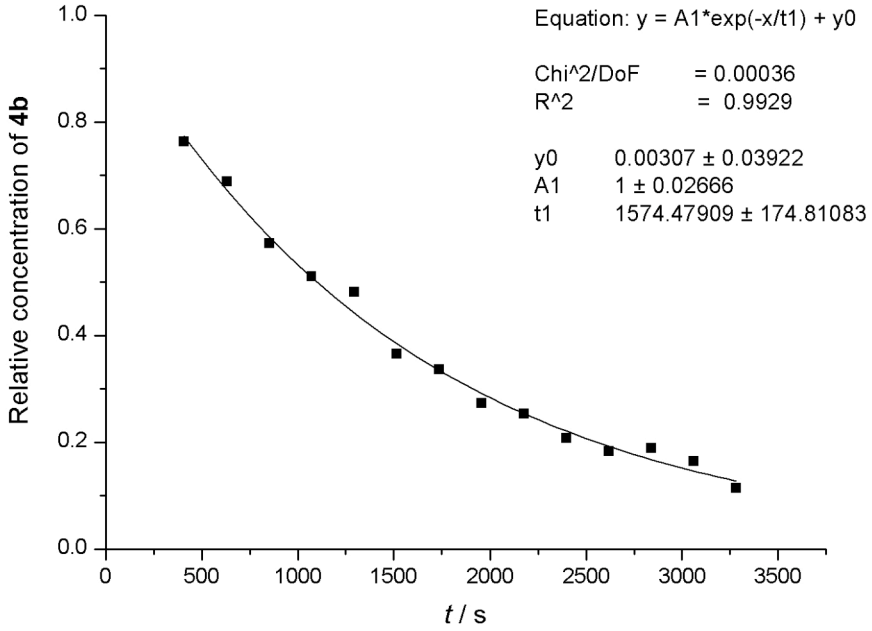

Figure S4: Typical exponential fit; corresponds to entry 7 in Table S1.

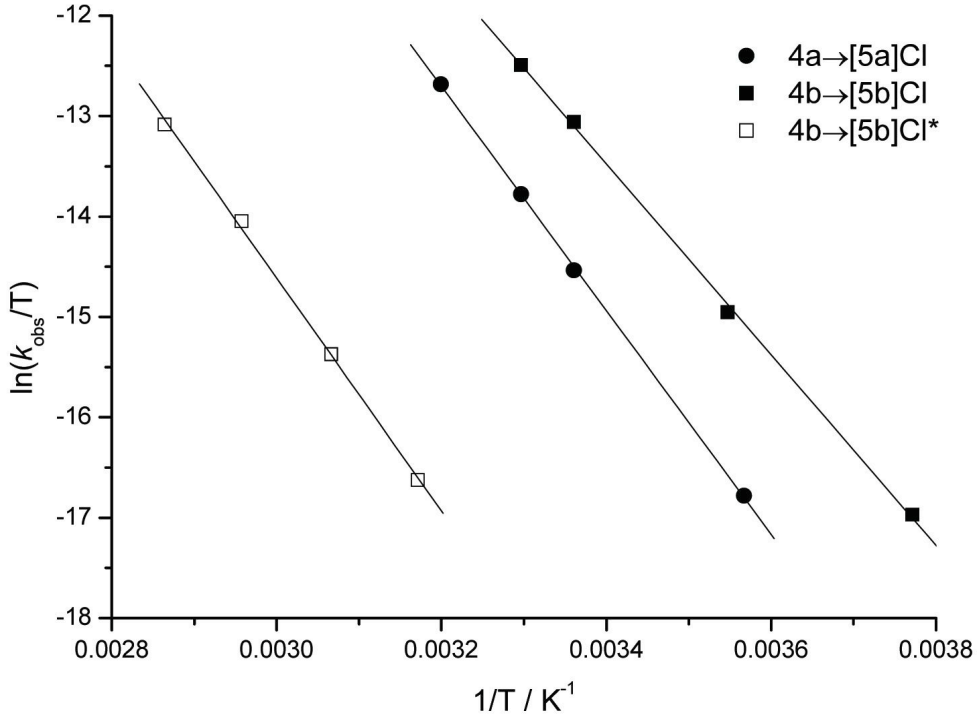

Figure S5: Eyring plot for chelation of reactions of **4a** (R^2 = 1.000) and **4b** (R^2 = 0.999) in 1:1 MeOH-CH_2ClCH_2Cl and **4b** (R^2 = 0.999) in CH_2ClCH_2Cl (indicated by asterisk).

Table S2: Rate constants for chelation reactions of **4a** and **4b** at different pressures.[a]

		ligand	solvent (v/v)	P / bar	$10^4 \cdot k_{obs}$ / s^{-1}	R^2_{fit}
1	**4a→[5a]Cl**	dppm	1:1 MeOH-CH_2ClCH_2Cl	1	1.353 ± 0.002	1.000
2		dppm	1:1 MeOH-CH_2ClCH_2Cl	504	1.310 ± 0.003	1.000
3		dppm	1:1 MeOH-CH_2ClCH_2Cl	1003	1.239 ± 0.003	1.000
4		dppm	1:1 MeOH-CH_2ClCH_2Cl	1507	1.150 ± 0.003	1.000
5	**4b→[5b]Cl**	dppv	1:1 MeOH-CH_2ClCH_2Cl	1	5.774 ± 0.009	1.000
6		dppv	1:1 MeOH-CH_2ClCH_2Cl	248	6.300 ± 0.012	1.000
7		dppv	1:1 MeOH-CH_2ClCH_2Cl	486	6.43 ± 0.02	1.000
8		dppv	1:1 MeOH-CH_2ClCH_2Cl	748	6.873 ± 0.012	1.000
9		dppv	1:1 MeOH-CH_2ClCH_2Cl	997	6.88 ± 0.03	1.000
10		dppv	1:1 MeOH-CH_2ClCH_2Cl	1250	7.18 ± 0.03	1.000

[a] Errors quoted are the standard errors calculated from the exponential fitting.

4. Kinetic studies of [2a-e]PF_6

Table S3: Rate constants for chelation reactions of **[2a-e]PF_6** at different temperatures.[a]

		ligand	solvent	T / K	$10^4 \cdot k_{obs}$ / s^{-1}	R^2_{fit}
1	**[2a]PF_6→[5a]PF_6**	dppm	CH_2ClCH_2Cl	326.7	0.141 ± 0.005	0.998
2		dppm	CH_2ClCH_2Cl	331.6	0.240 ± 0.009	0.998
3		dppm[b]	CH_2ClCH_2Cl	343.4	0.93 ± 0.03	0.999
4		dppm	CH_2ClCH_2Cl	349.1	2.39 ± 0.03	0.998
5		dppm	CH_2ClCH_2Cl	353.0	3.7 ± 0.3	0.994
6	**[2b]PF_6→[5b]PF_6**	dppv	CH_2ClCH_2Cl	327.2	0.147 ± 0.008	0.997
7		dppv	CH_2ClCH_2Cl	333.5	0.33 ± 0.02	0.997
8		dppv	CH_2ClCH_2Cl	343.7	1.13 ± 0.10	0.994
9		dppv	CH_2ClCH_2Cl	352.6	3.8 ± 0.3	0.997
10	**[2c]PF_6→[5c]PF_6**	dppe	CH_2ClCH_2Cl	332.7	0.215 ± 0.009	0.999
11		dppe	CH_2ClCH_2Cl	343.5	1.15 ± 0.07	0.997
12		dppe	CH_2ClCH_2Cl	354.3	4.6 ± 0.2	0.998
13	**[2d]PF_6→[5d]PF_6**	dppp	CH_2ClCH_2Cl	332.1	0.28 ± 0.02	0.998
14		dppp	CH_2ClCH_2Cl	343.1	1.31 ± 0.06	0.998
15		dppp	CH_2ClCH_2Cl	354.3	6.1 ± 0.2	0.999
16	**[2e]PF_6→[5e]PF_6**	dppf	CH_2ClCH_2Cl	295.0	0.027 ± 0.007	0.999
17		dppf	CH_2ClCH_2Cl	308.9	0.31 ± 0.02	0.999
18		dppf	CH_2ClCH_2Cl	320.0	1.9 ± 0.2	0.996
19		dppf	CH_2ClCH_2Cl	332.5	9.5 ± 0.7	0.996

[a] Errors quoted are the standard errors calculated from the exponential fitting. [b] Excluded from Erying fit.

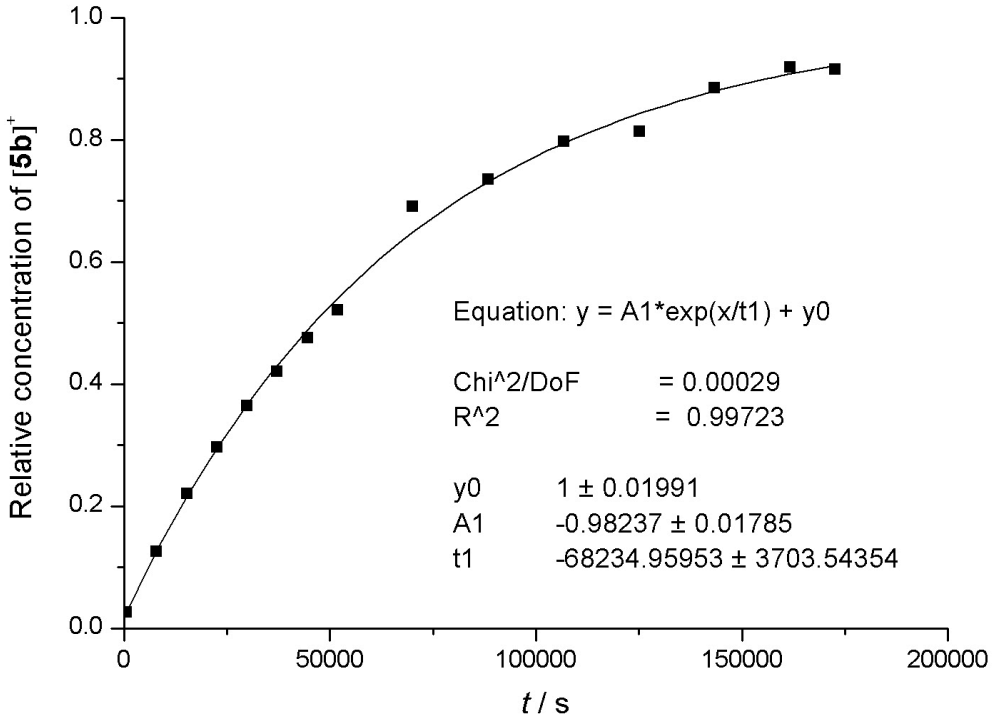

Figure S6: Typical exponential fit; corresponds to entry 6 in Table S3.

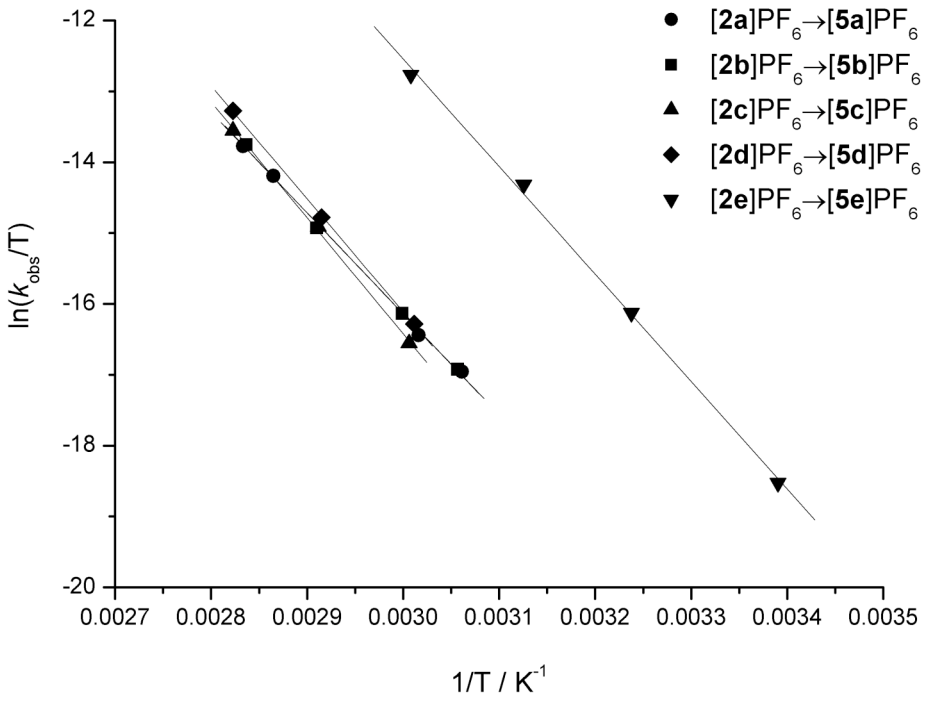

Figure S7: Eyring plot for the chelation of complexes **[2]PF$_6$** in CH_2ClCH_2Cl (**[2e]PF$_6$** R^2 = 0.998).

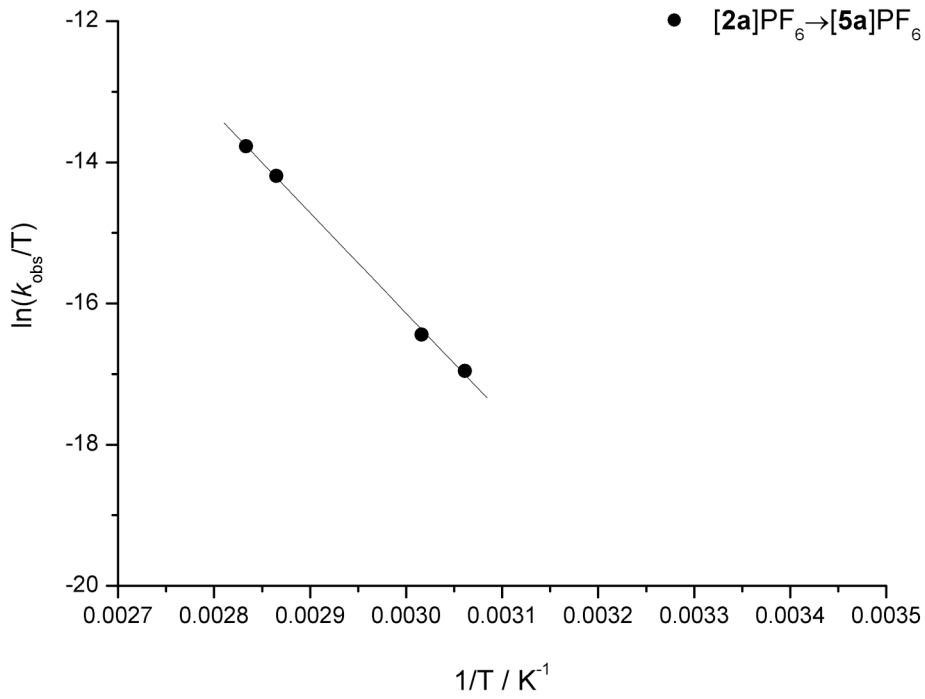

Figure S8: Eyring plot for the chelation of **[2a]PF$_6$** in CH_2ClCH_2Cl ($R^2 = 0.999$).

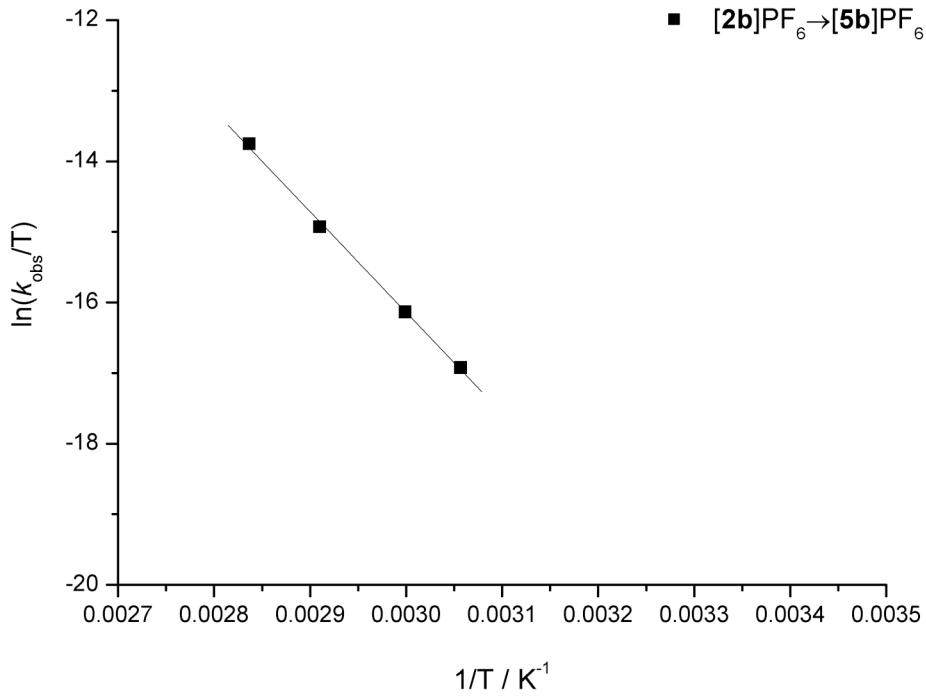

Figure S9: Eyring plot for the chelation of **[2b]PF$_6$** in CH_2ClCH_2Cl ($R^2 = 0.998$).

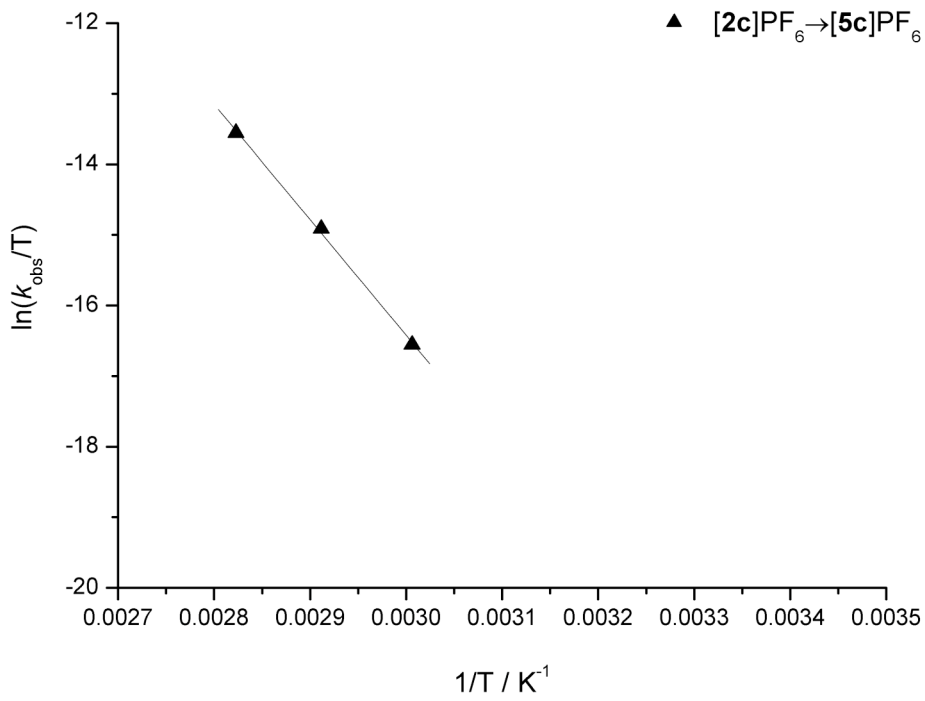

Figure S10: Eyring plot for the chelation of **[2c]PF$_6$** in CH_2ClCH_2Cl ($R^2 = 0.999$).

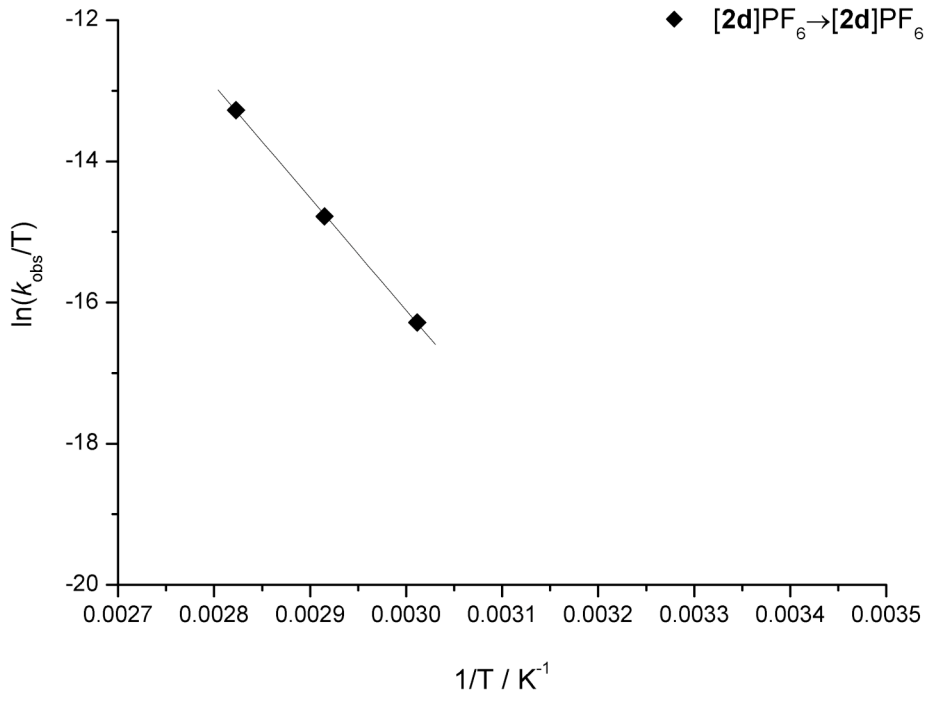

Figure S11: Eyring plot for the chelation of **[2d]PF$_6$** in CH_2ClCH_2Cl ($R^2 = 1.000$).