Supplementary Material (ESI) for *Dalton Transactions*

Controlling the Extent of Pi-Backbonding in Platinum(II) Terpyridyl Systems. A Detailed Kinetic, Mechanistic and Computational Approach

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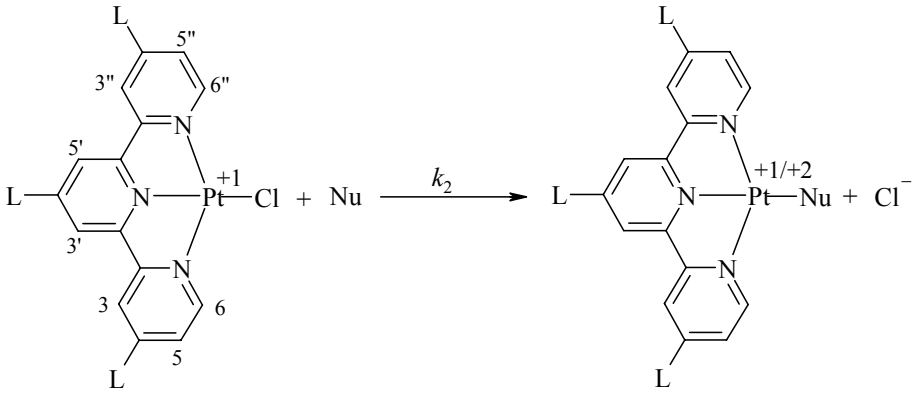
Reaction Scheme



L = H (**Pt1**) or ^{t}Bu (**Pt2**); Nu = TU, DMTU, TMTU, I^-, SCN^-

Table S1 Summary of selected wavelengths (nm) used in kinetic studies

Nucleophile	$[Pt(terpy)Cl]^+$ (Pt1)	$[Pt(^tBu_3terpy)Cl]^+$ (Pt2)
TU	334[1]	385
DMTU	335[1]	395
TMTU	409[1]	415
I^-	344	422
SCN^-	290	389

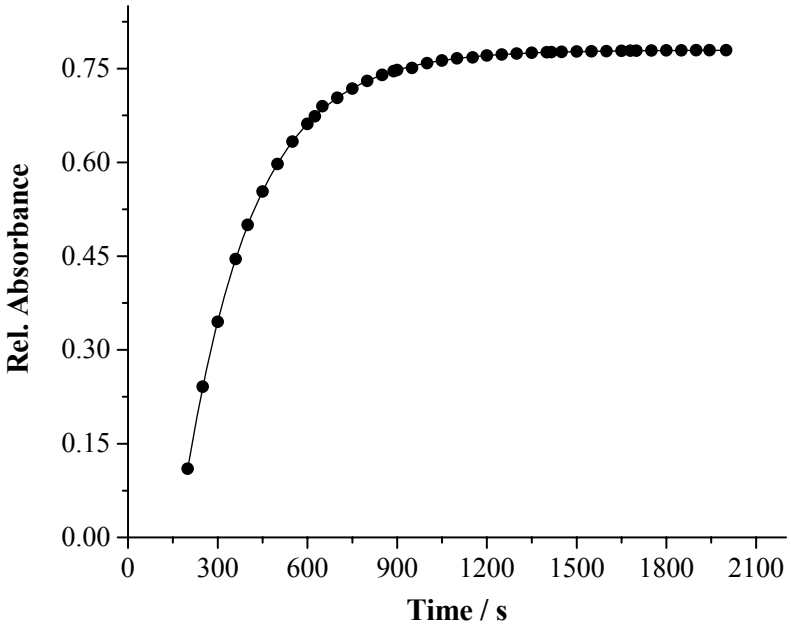


Figure S1 Kinetic trace and single order exponential fit for the reaction of **Pt2** (0.170 mM) with thiocyanate (SCN^-, 1.699 mM) in methanol followed at 389 nm, I = 0.1 M ($NaClO_4$), T = 298.15 K.

Table S2 Average observed rate constants, k_{obs}[a], at 25.0°C for reactions of **Pt1** (0.05 mM) with a series of neutral nucleophiles at different nucleophile concentrations.[1]

[TU] / mM	k_{obs} / s^{-1}	[DMTU] / mM	k_{obs} / s^{-1}	[TMTU] / mM	k_{obs} / s^{-1}
0.556	0.810	0.555	0.234	0.551	0.066
1.111	1.644	1.110	0.501	1.110	0.096
1.667	2.568	1.664	0.683	1.665	0.137
2.223	3.295	2.219	0.982	2.220	0.161
2.779	4.135	2.774	1.289	2.775	0.238

[a] Taken as an average of at least 6 kinetic runs with a SD between 0.3 and 5%.

Table S3 Average observed rate constants, k_{obs}[a], at 25.0°C for reactions of **Pt1** (13.3 μM (I^-); 14.6 μM (SCN^-)) with a series of ionic nucleophiles at different nucleophile concentrations

[I^-] / mM	**k_{obs} / s^{-1}**	**[SCN^-] / mM**	**k_{obs} / s^{-1}**
0.137	0.0268	0.148	2.247×10^{-3}
0.274	0.0621	0.296	4.747×10^{-3}
0.410	0.0991	0.444	7.556×10^{-3}
0.547	0.132	0.592	0.0103
0.684	0.170	0.740	0.0129

[a] Taken as an average of 10 kinetic runs with a SD between 0.3 and 5%.

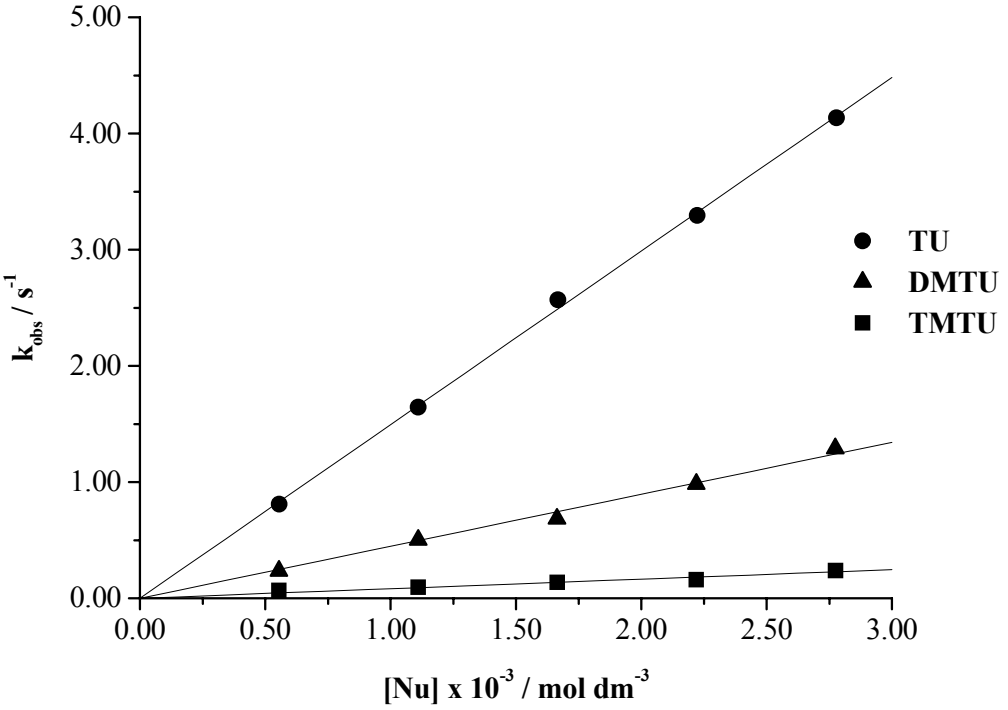


Figure S2 Dependence of the pseudo first-order rate constants (k_{obs}) on the entering nucleophile concentration for chloride substitution on **Pt1** (0.05 mM) in methanol, I = 0.1 M ($LiCF_3SO_3$), T = 298.15K.[1]

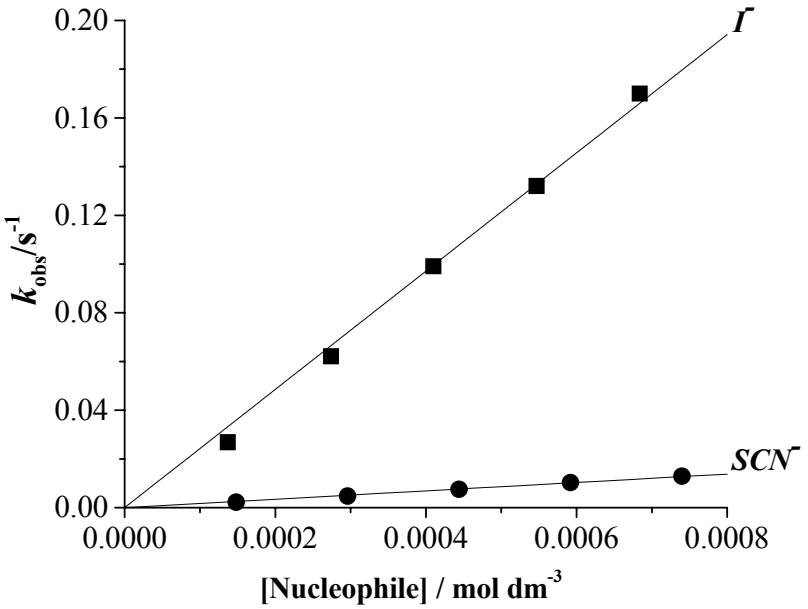


Figure S3 Dependence of the pseudo first-order rate constants (k_{obs}) on the entering nucleophile concentration for chloride substitution on **Pt1** (13.3 μM (I^-); 14.6 μM (SCN^-)) in methanol, I = 0.1 M ($LiCF_3SO_3$), T = 298.15K.

Table S4 Average observed rate constants, k_{obs}[a], at 25.0°C for reactions of **Pt2** (*ca.* 0.165 mM (TU, DMTU, TMTU); 0.170 mM (I^-, SCN^-)) with a series of neutral and ionic nucleophiles at different nucleophile concentrations.

[TU] (mM)	k_{obs} / s^{-1}	[DMTU] (mM)	k_{obs} / s^{-1}	[TMTU] (mM)	k_{obs} / s^{-1}	[I^-] (mM)	k_{obs} / s^{-1}	[SCN^-] (mM)	k_{obs} / s^{-1}
1.625	0.674	1.615	0.239	1.641	0.0598	1.709	0.0978	1.699	4.331×10^{-3}
3.250	1.401	3.229	0.487	3.282	0.121	3.418	0.200	3.397	9.361×10^{-3}
4.875	2.172	4.844	0.707	4.923	0.184	5.128	0.304	5.096	0.0145
6.500	2.969	6.458	0.988	6.564	0.248	6.837	0.407	6.794	0.0195
8.125	3.717	8.073	1.236	8.205	0.312	8.546	0.518	8.493	0.0248

[a] Taken as an average of 10 kinetic runs with a SD between 0.3 and 5%.

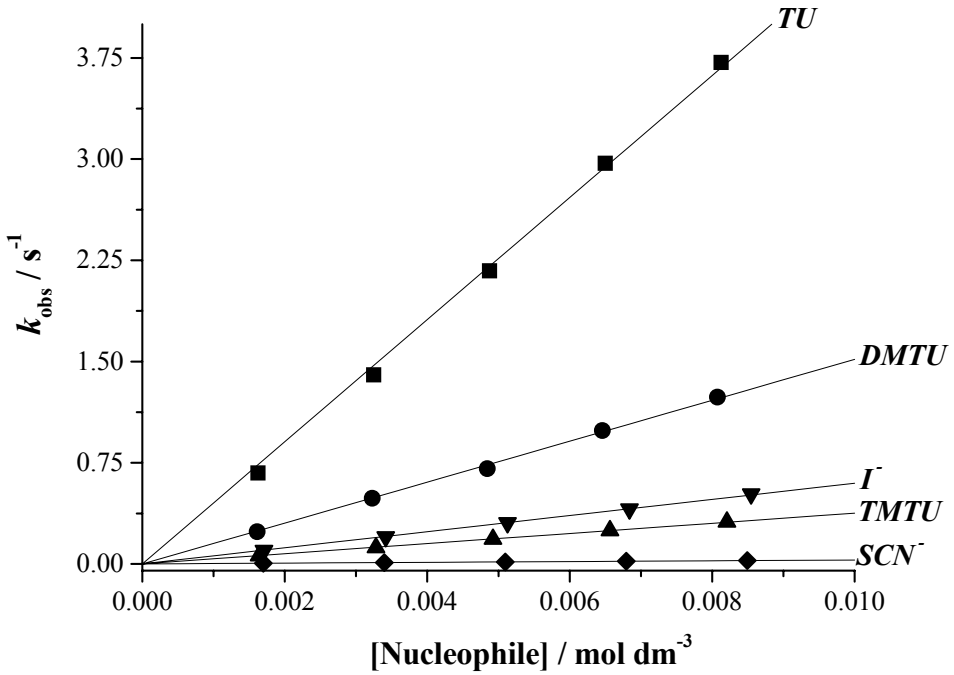


Figure S4 Dependence of the pseudo first-order rate constants (k_{obs}) on the entering nucleophile concentration for chloride substitution on **Pt2** (*ca.* 0.170 mM) in methanol, I = 0.1 M ($NaClO_4$), T = 298.15K.

Table S5 Average observed rate constants, k_{obs}[a], at varied temperatures for reactions of **Pt1** (0.05 mM) with a series of different nucleophiles whilst maintaining nucleophile concentrations at ≈ 30x [Pt1]. [TU] = 1.67 mM; [DMTU] = 1.66 mM, [TMTU] = 1.66 mM.[1]

T (K)	TU, k_{obs}(s^{-1})	DMTU, k_{obs}(s^{-1})	TMTU, k_{obs}(s^{-1})
288.15	1.569	0.411	0.087
293.15	2.026	0.531	0.108
298.15	2.568	0.683	0.137
303.15	2.934	0.947	0.195
308.15	3.754	1.171	0.231

[a] Taken as an average of at least 6 kinetic runs with a SD between 0.1 and 2%.

Table S5 Average observed rate constants, k_{obs}[a], at varied temperatures for reactions of **Pt1** (13.3 μM (I^-); 14.6 μM (SCN^-)) with a series of ionic nucleophiles whilst maintaining nucleophile concentrations at ≈ 30x [Pt1]. [I^-] = 0.410 mM; [SCN^-] = 0.444 mM.

T (K)	I^-, $k_{obs}(s^{-1})$	SCN^-, $k_{obs}(s^{-1})$
288.3	0.0500	3.756×10^{-3}
293.2	0.0695	5.312×10^{-3}
298.2	0.0991	7.556×10^{-3}
303.2	0.137	0.0105
308.2	-	0.0146

[a] Taken as an average of 10 kinetic runs with a SD between 0.1 and 2%.

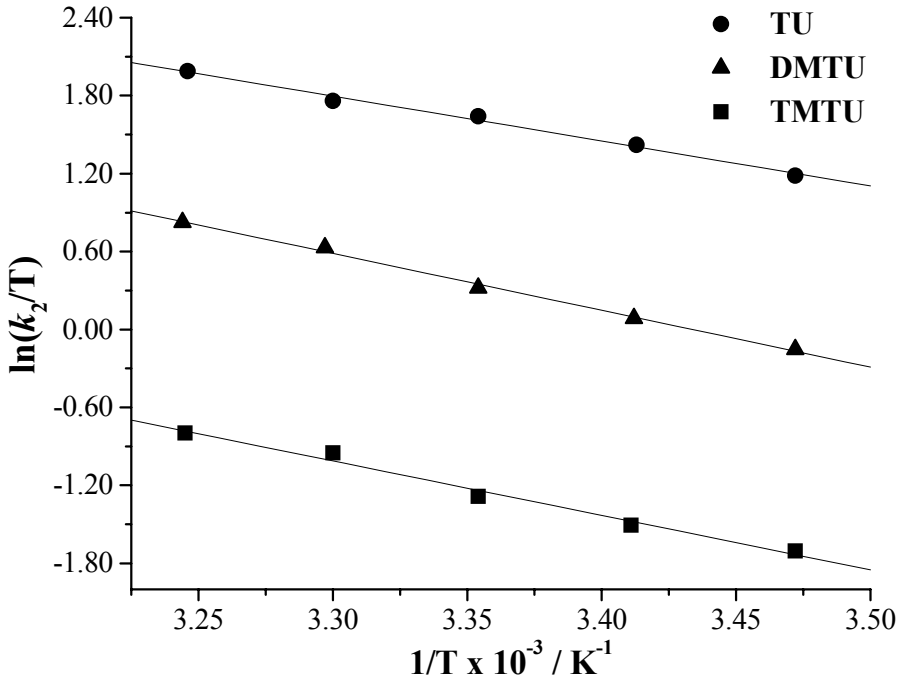


Figure S5 Plots of ln(k_2/T) versus 1/T for the reaction of **Pt1** (0.05 mM) with a series of neutral nucleophiles at various temperatures in the temperature range 15 to 35 °C whilst maintaining nucleophile concentrations at ≈ 30x [Pt1].[1]

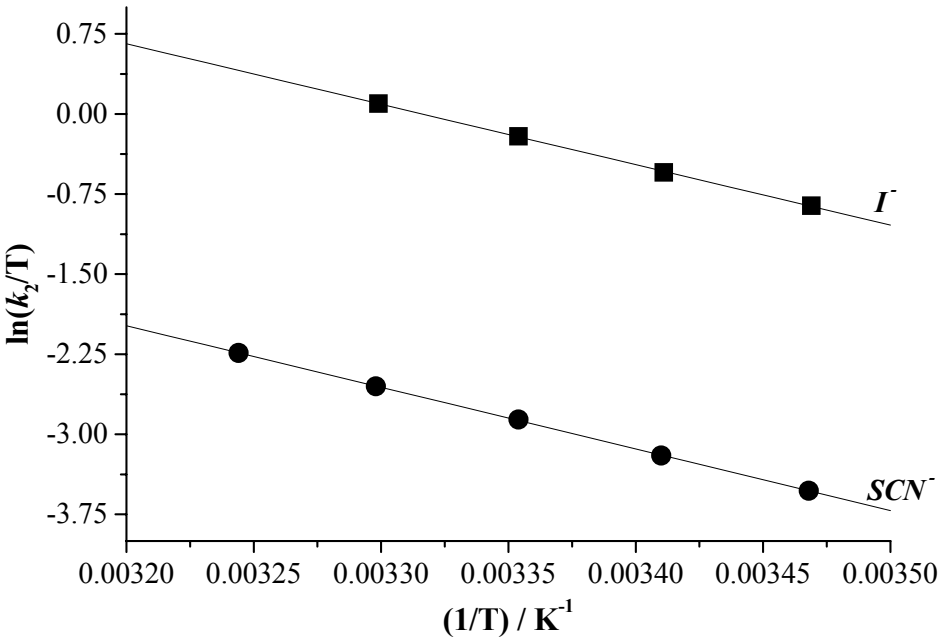


Figure S6 Plots of ln(k_2/T) versus 1/T for the reaction of **Pt1** (13.3 μM (I^-); 14.6 μM (SCN^-)) with the ionic nucleophiles at various temperatures in the temperature range 15 to 35 °C whilst maintaining nucleophile concentrations at ≈ 30x [Pt1].

Table S5 Average observed rate constants, k_{obs}[a], at varied temperatures for reactions of **Pt2** (0.170 mM) with a series of different nucleophiles whilst maintaining nucleophile concentrations at ≈ 30x [Pt2]. [TU] = 4.875 mM; [DMTU] = 4.844 mM, [TMTU] = 4.923 mM, [I^-] = 5.128, [SCN^-] = 5.096 mM.

T (K)	TU k_{obs}(s^{-1})	DMTU k_{obs}(s^{-1})	TMTU k_{obs}(s^{-1})	I^- k_{obs} (s^{-1})	SCN^- k_{obs} (s^{-1})
288.15	1.318	0.387	0.107	0.150	6.366×10^{-3}
293.15	1.698	0.507	0.141	0.214	9.740×10^{-3}
298.15	2.172	0.707	0.184	0.304	0.0145
303.15	2.772	0.938	0.235	0.428	0.0215
308.15	3.516	1.188	0.300	0.596	0.0316

[a] Taken as an average of 10 kinetic runs with a SD between 0.1 and 2%.

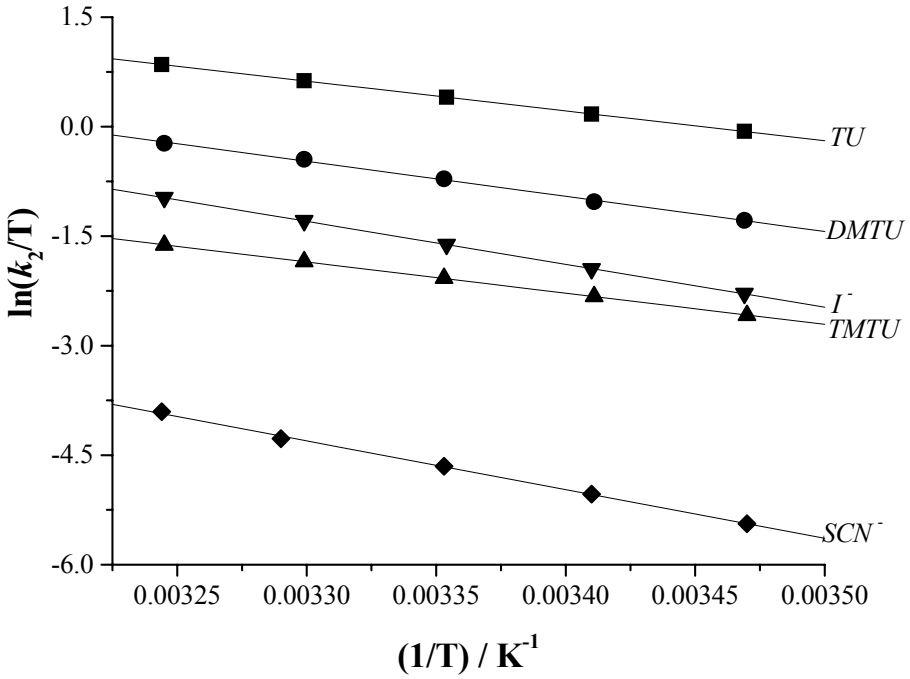


Figure S7 Plots of ln(k_2/T) versus 1/T for the reaction of **Pt2** (0.170 mM) with a series of neutral and ionic nucleophiles at various temperatures in the temperature range 15 to 35 °C whilst maintaining nucleophile concentrations at ≈ 30x [Pt2].

Table S6 Energies of the LUMO and LUMO + 1 for terpy derivatives, as calculated by Cummings *et al*.[2]

Compound	**LUMO (eV)**	**LUMO + 1 (eV)**
$^{t}Bu_3$terpy	-0.74	-0.37
terpy	-0.82	-0.44
Cl-terpy	-0.97	-0.58
Cl_3-terpy	-1.15	-0.77

Table S7 Correlation of observed X-ray data with DFT-calculated data for the complexes $[Pt(terpy)(OMe)]^+$ and $[Pt(^tBu_3terpy)Cl]^+$.[3,4]

Complex	Bond Lengths (Calcd., Obsd.) / Å			
$[Pt(terpy)(OMe)]^+$	*Pt–N1*	*Pt–N2*	*Pt–N3*	*Pt–O*
	1.98, 1.92	2.05, 2.10	2.05, 2.04	2.00, 2.00
$[Pt(^tBu_3terpy)Cl]^+$	*Pt–N1*	*Pt–N2*	*Pt–N3*	*Pt–Cl*
	1.963, 1.935	2.050, 2.020	2.050, 2.025	2.352, 2.288

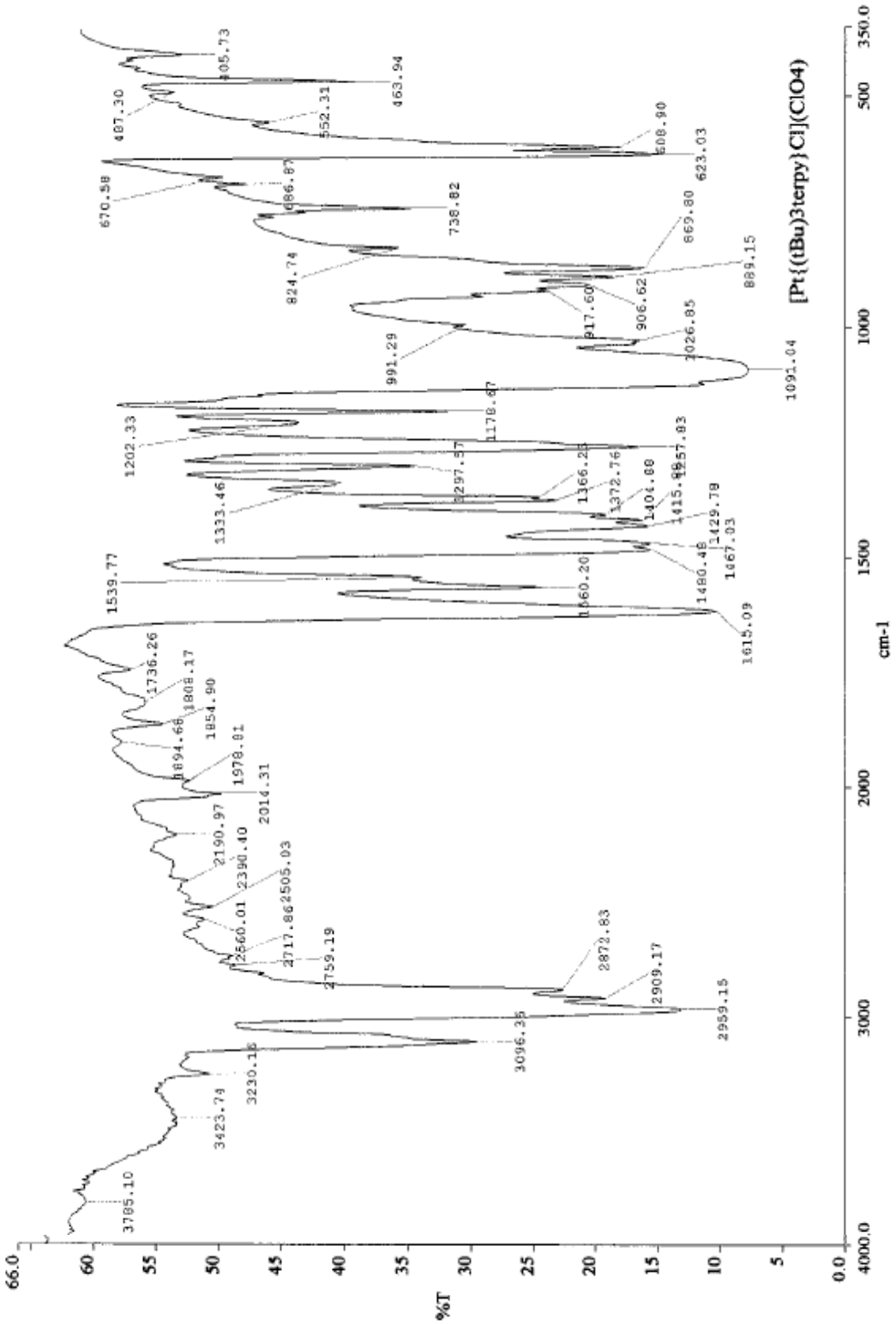
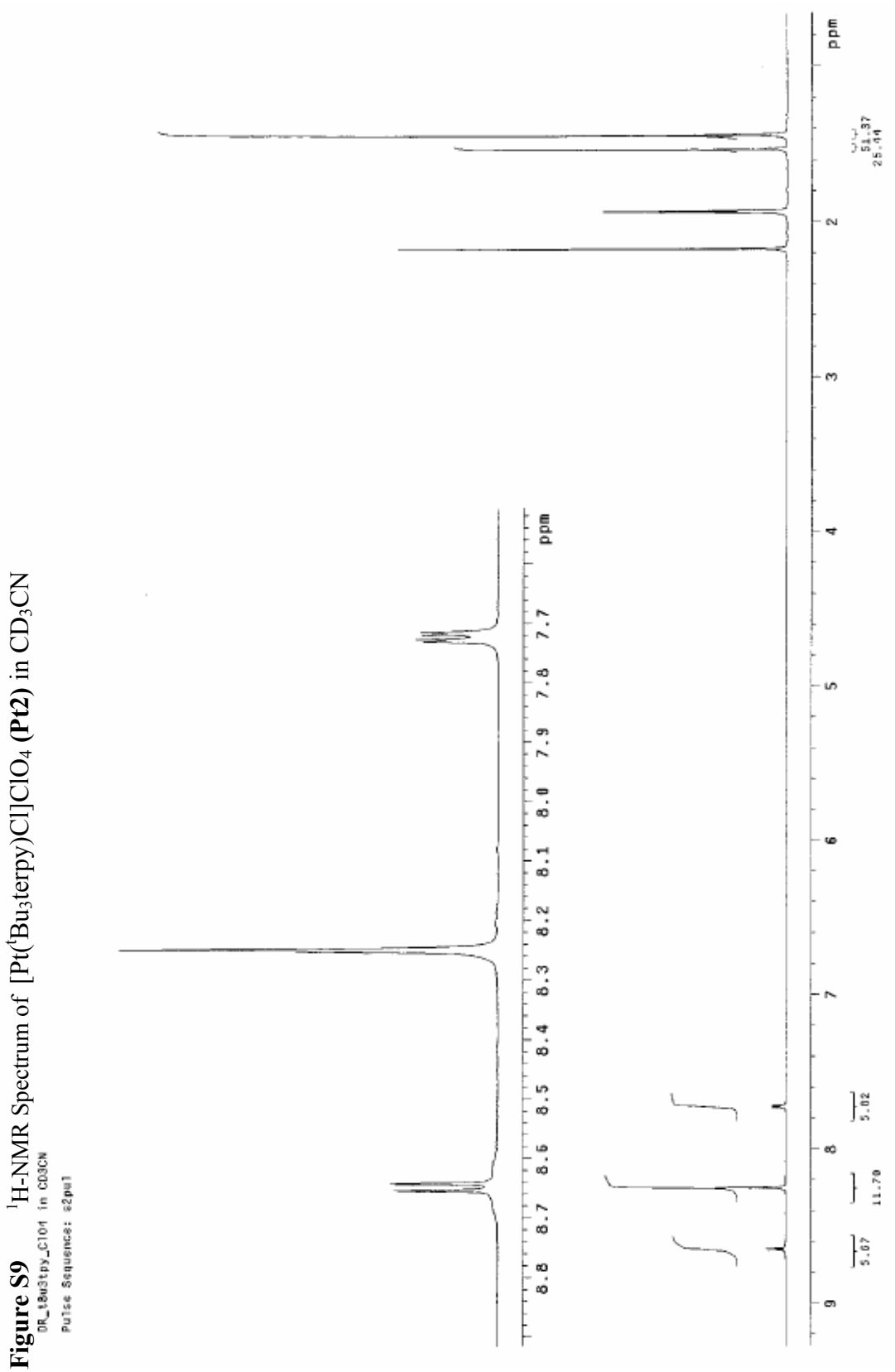


Figure S8 Infrared spectrum of [Pt(^{t}Bu$_3$terpy)Cl]ClO$_4$ **(Pt2)** in KBr.

Figure S9 ^{1}H-NMR Spectrum of [Pt(^{t}Bu$_3$terpy)Cl]ClO$_4$ **(Pt2)** in CD_3CN



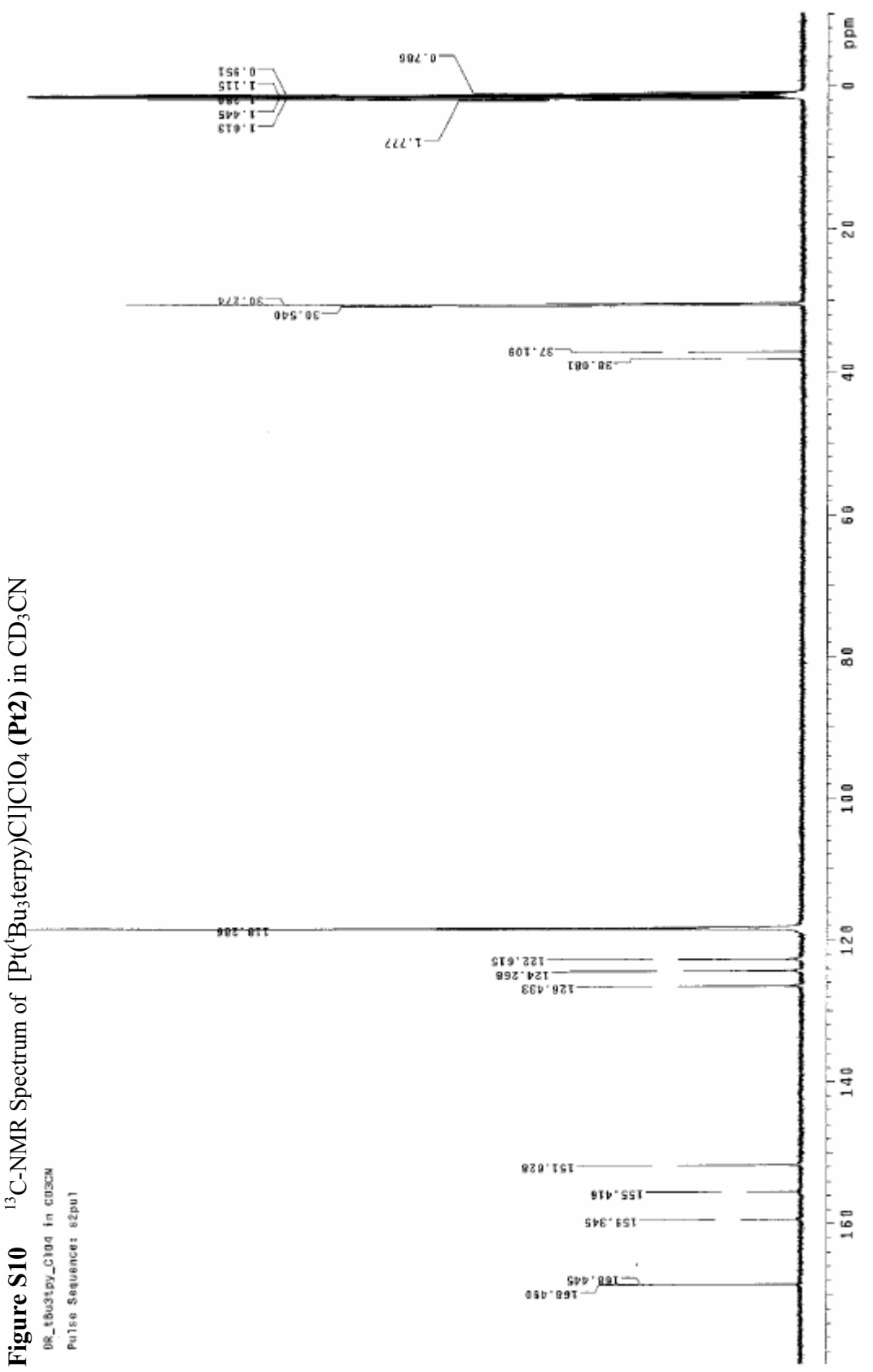
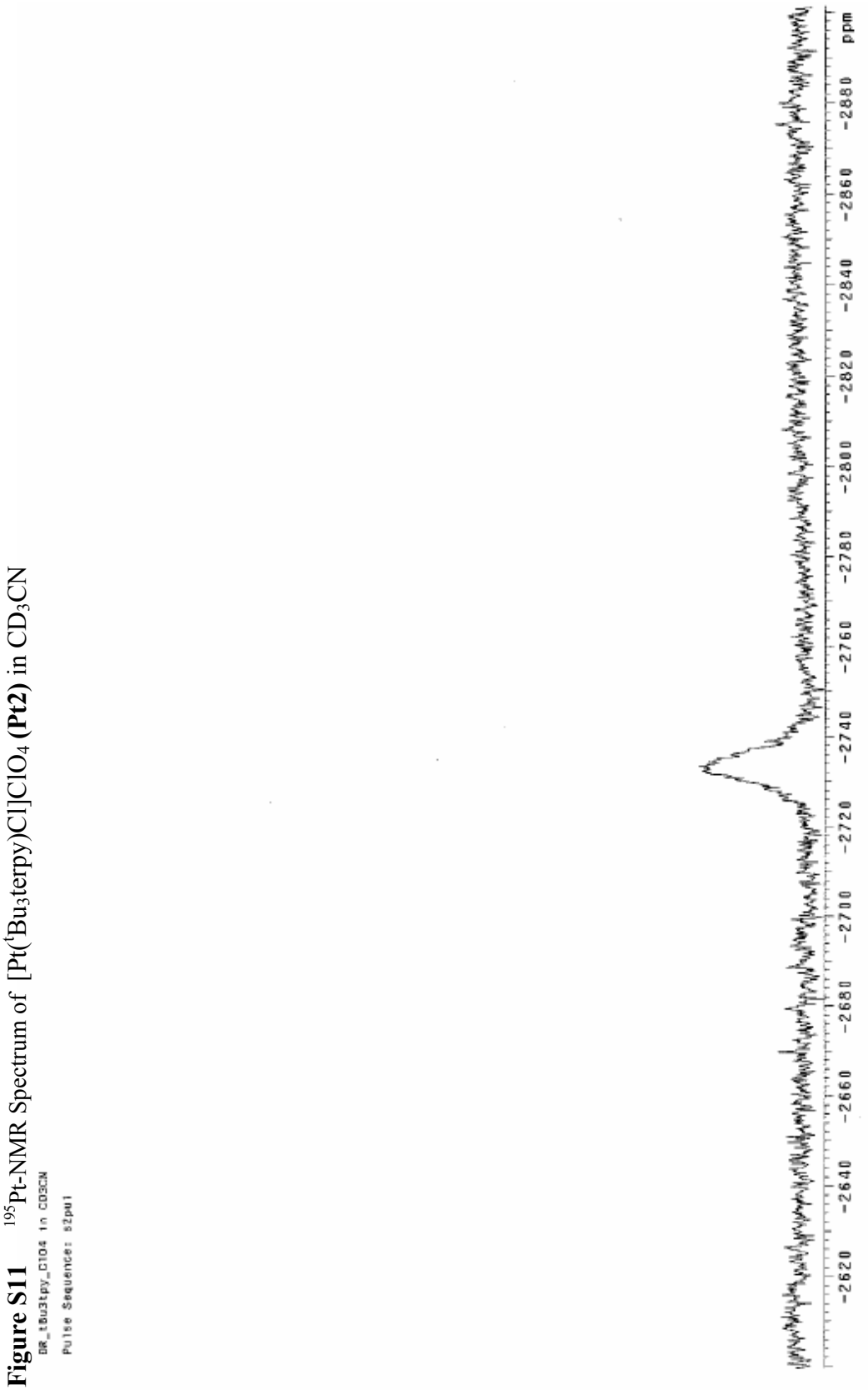


Figure S10 ^{13}C-NMR Spectrum of [Pt(^{t}Bu$_3$terpy)Cl]ClO$_4$ **(Pt2)** in CD$_3$CN

Figure S11 ^{195}Pt-NMR Spectrum of [Pt(^{t}Bu$_3$terpy)Cl]ClO$_4$ **(Pt2)** in CD_3CN



References

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