Supporting Information

Photophysics and Electrochemistry of a Platinum-Acetylide Disubstituted Perylenediimide

Ben A. Llewellyn,[a] Anna G. Slater,[a] Gudrun Goretzki,[a] Timothy L. Easun,[a] E. Stephen Davies,[a] Stephen P. Argent,[a] William Lewis,[a] Andrew Beeby,[b] Michael W. George[a] and Neil. R. Champness[a]*

Electrochemistry Measurements.

Compound	1st reduction	2nd reduction	Oxidation	$\Delta E(Fc^+/Fc)$
1	-1.22 (0.10)	-1.46 (0.09)	+0.71[#]	(0.08)
2	-1.21 (0.08)	-1.44 (0.07)	+0.72[#]	(0.08)

Potentials reported as $E_{1/2}$ (= $(E_p^a + E_p^c)/2$) in V vs. Fc^+/Fc at 0.1 Vs^{-1} scan rate and quoted to the nearest 0.01 V. Values in parentheses are ΔE (= $E_p^a - E_p^c$) for the couple at 0.01 Vs^{-1}. [#] Peak maximum from square wave voltammetry

EPR Measurements for reduced species.

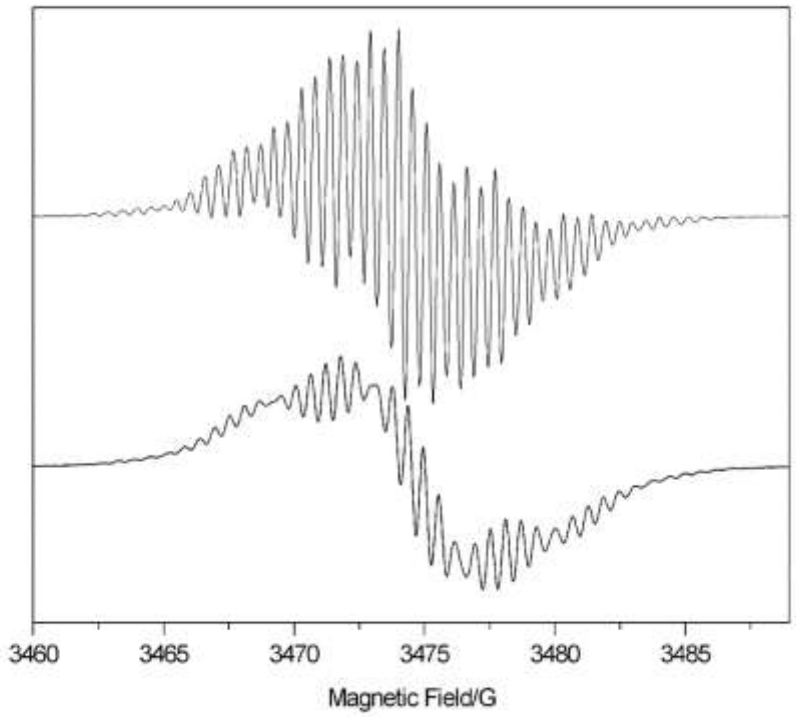


Figure S1. Experimental EPR spectra for electrochemically generated $[\mathbf{1}]^-$ (upper trace, g_{iso} 2.0044) and $[\mathbf{2}]^-$ (lower trace, g_{iso} 2.0043) in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) at ambient temperature.

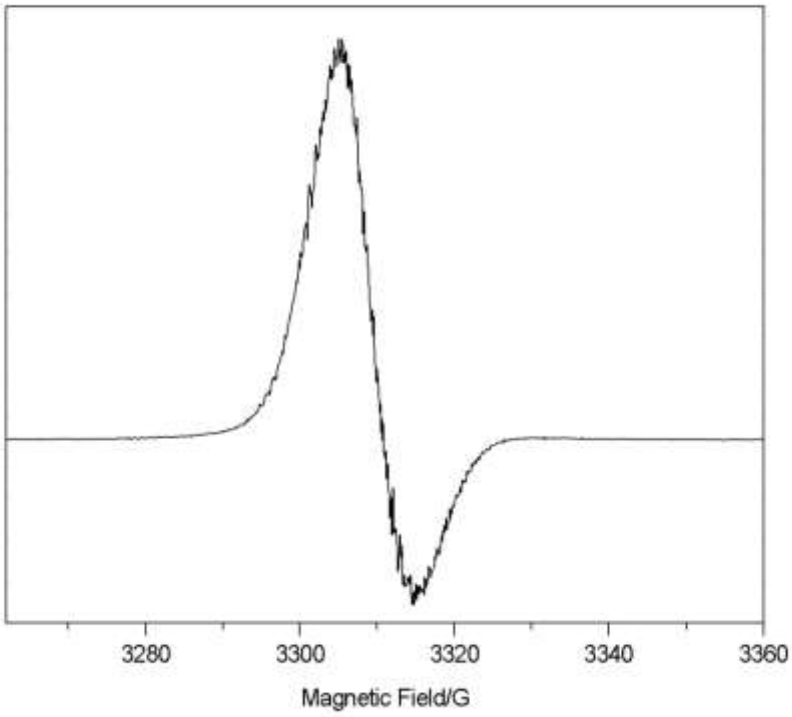


Figure S2. Experimental EPR spectrum for electrochemically generated [**2**]$^{-}$ in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) as a frozen glass at 77 K.

Spectroelectrochemistry Measurements.

Table S2. UV-visible data obtain from spectroelectrochemistry measurements.

Compound	λ_{max}/nm (εx 10^{-4}/moldm^{-3}cm^{-1})
[**1**]^{0}	263 (3.0), 284 (2.9), 325 (3.6), 443 (1.0), 578 (1.2), 629 (2.0)
[**1**]$^{1-}$	257 (4.3), 325 (2.8), 504 (0.9), 771 (2.8), 855 (1.7)
[**1**]$^{2-}$	259 (4.1), 287 (3.8), 325 (2.4), 364 (2.0), 447 (0.4), 610 (3.0), 640 (3.1)
[**1**]$^{1+b}$	286 (2.8), 318 (3.7), 468 (1.4), 577 (1.3), 613 (1.4)
[**2**]^{0}	265 (7.9), 284 (8.0), 326 (8.5), 446 (2.3), 582 (3.2), 628 (4.6)
[**2**]$^{1-}$	262 (10.4), 325 (6.9), 507 (2.0), 769 (7.3), 853 (4.1)
[**2**]$^{2-}$	262 (10.0), 286 (10.2), 325 (5.9), 361 (4.8), 442 (0.9), 605 (7.7), 632 (7.9), 665 (4.4)

[a] obtained at a optically transparent electrode cell, in CH_2Cl_2 containing [$^{n}Bu_4N][BF_4$] (0.4 M) at 273 K, spectral range: 230 – 900 nm. [b] at 243 K.

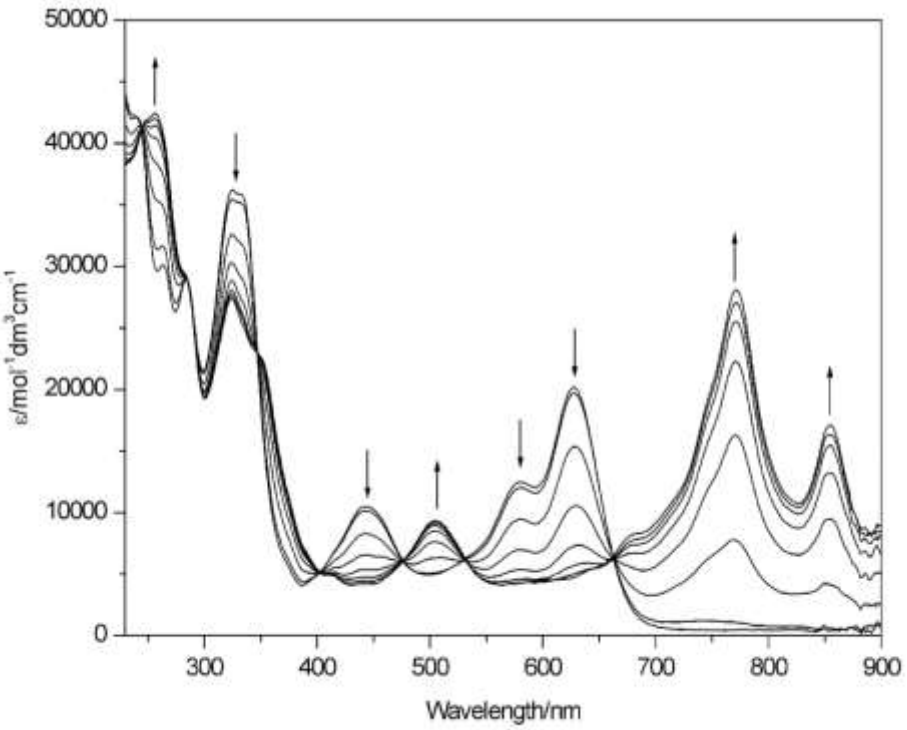


Figure S3. View of UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) using spectroelectrochemical methods for **1** at 273 K showing the inter-conversion of **1** to $[\mathbf{1}]^-$. Arrows indicate the progress of the reduction.

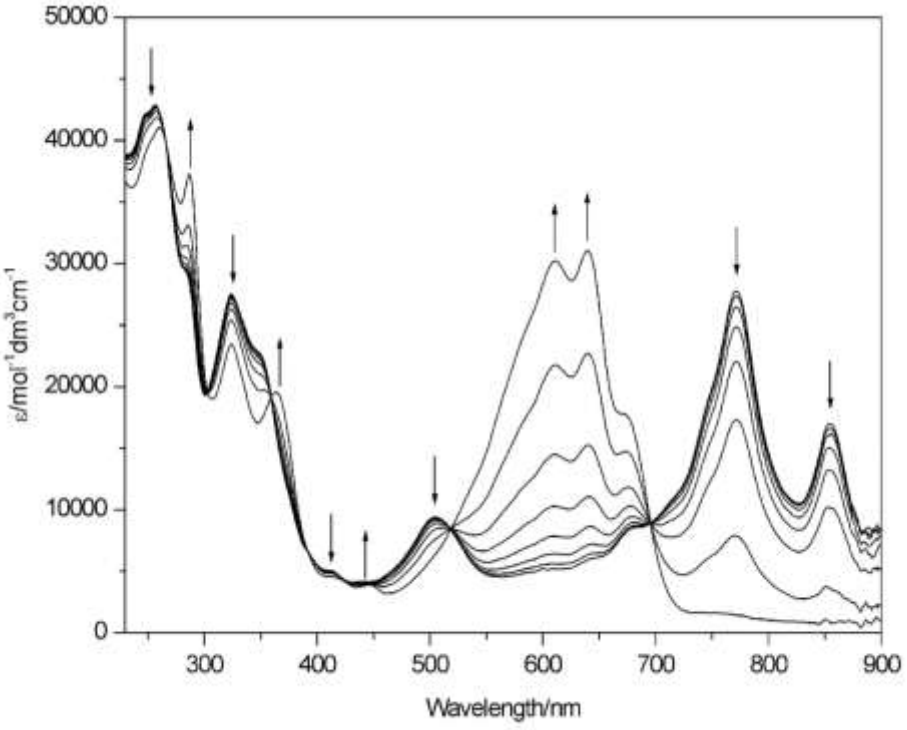


Figure S4. View of UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) using spectroelectrochemical methods for 1 at 273 K showing the inter-conversion of $[\mathbf{1}]^-$ to $[\mathbf{1}]^{2-}$. Arrows indicate the progress of the reduction.

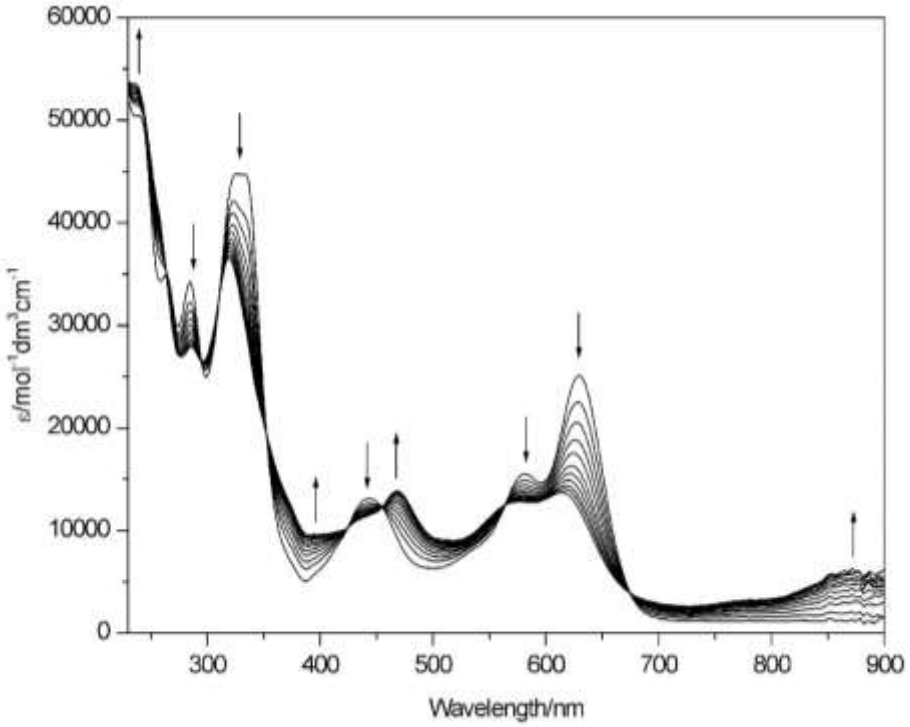
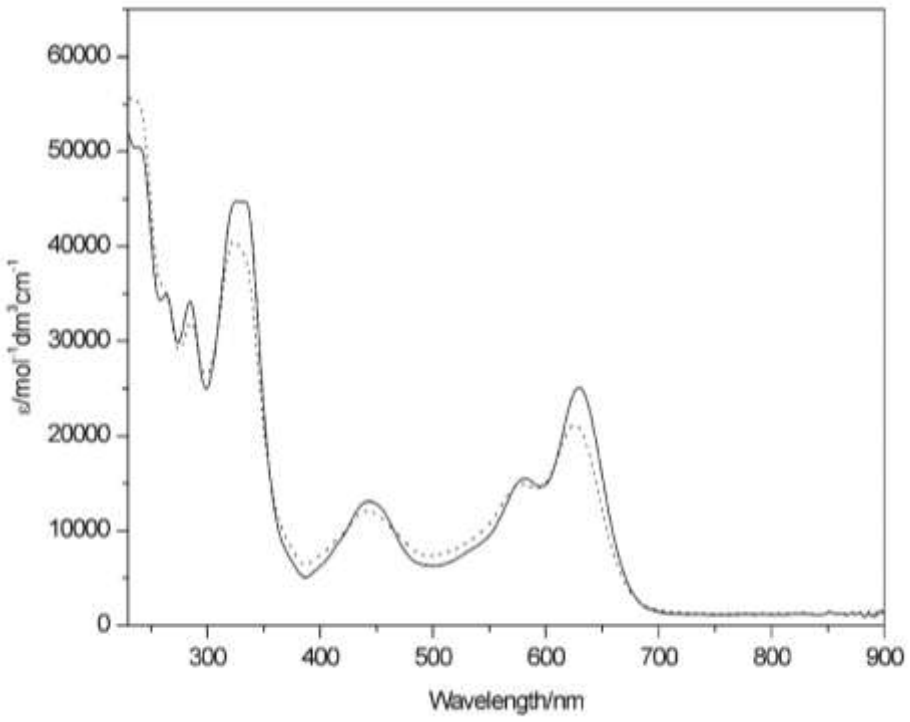


Figure S5. View of UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) using spectroelectrochemical methods for 1 at 243 K showing the inter-conversion of $[\mathbf{1}]^-$ to $[\mathbf{1}]^+$. Arrows indicate the progress of the oxidation**.**



UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.5 M) for **1** at 243 K before (solid line) and after (dotted line) oxidation to $[\mathbf{1}]^{1+}$.

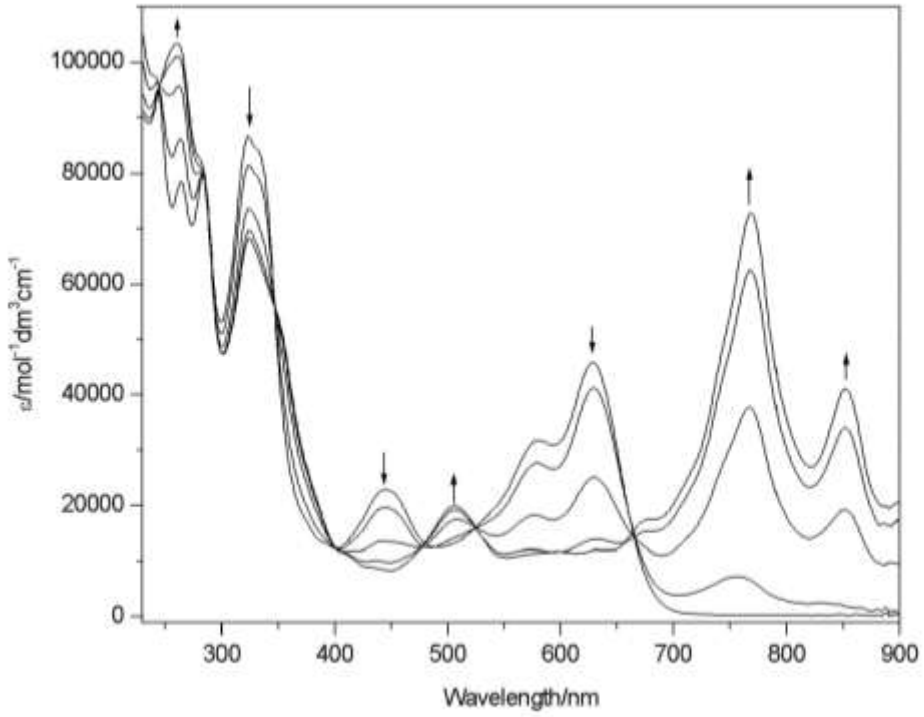


Figure S3. View of UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) using spectroelectrochemical methods for **2** at 273 K showing the inter-conversion of **2** to $[\mathbf{2}]^-$. Arrows indicate the progress of the reduction.

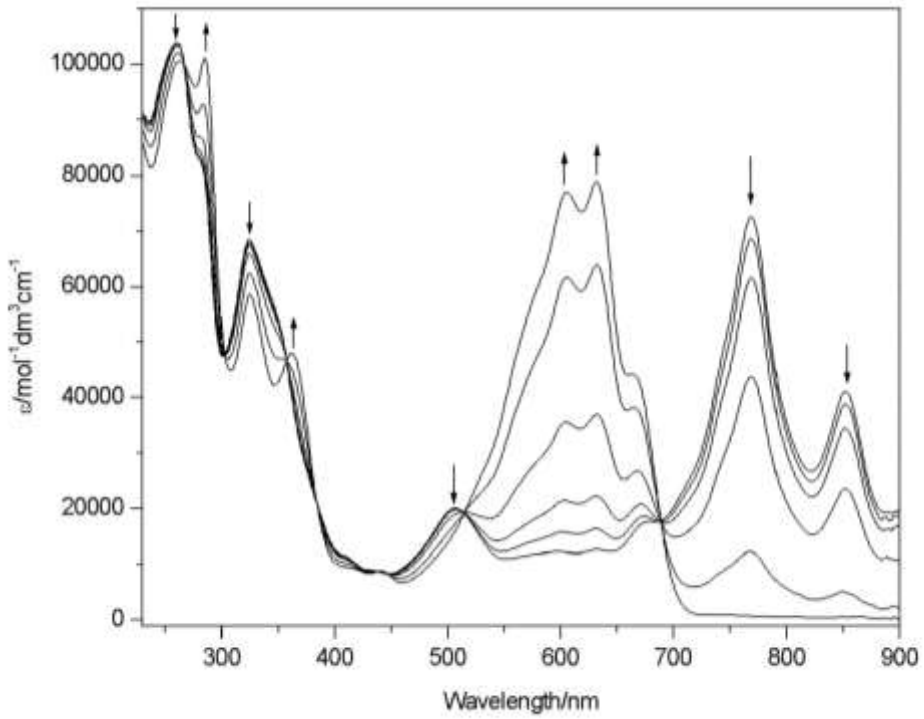


Figure S4. View of UV-visible spectra recorded in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) using spectroelectrochemical methods for **2** at 273 K showing the inter-conversion of $[\mathbf{2}]^-$ to $[\mathbf{2}]^{2-}$. Arrows indicate the progress of the reduction.

Compound	λ_{abs} / nm (ε / x10^3 M^{-1}cm^{-1})	λ_{em} / nm (r.t)	Φ_{em}	τ_{em} / ns	λ_{em} / nm (77 K)	τ_{em} / μs (77 K)
2	580 (31.5) 629 (45.7)	696	0.02	17	650 700	3.2
3	527 (19.9) 568 (28.8)	599 645 (sh)	0.70	6.9	-	-

Table 1 Photophysical properties of **2** and **3** at room temperature in dichloromethane and at 77 K in a propionitrile:butyronitrile (4:1) glass.

Synthesis of N,N`-Di-(*n*-butyl)-1,7-di(phenylethynl)perylene-3,4:9,10-tetracarboxylic diimide 3

N,N`-di-(*n*-butyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic bisimide (1.98 g, 3 mmol) was dissolved in a mixture of dry THF (100 mL) and dry triethylamine (50 mL) under an argon atmosphere. $PdCl_2(PPh_3)_2$ (84 mg, 0.12 mmol), CuI (29 mg, 0.15 mmol) and phenylacetylene (1.3 mL, 12 mmol) were added and the reaction mixture was stirred at 80°C for 4 h, before being cooled to room temperature and poured into HCl (0.1 M, 100 mL). The product was extracted with dichloromethane and the organic layer washed with water until neutral, dried with Na_2SO_4 and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, $CHCl_3$) to give 1.77 g (84%) of a red powder. MS (MALDI-TOF): *m/z* 702.5 (M). ^{1}H NMR ($CDCl_3$): δ = 10.09 (d, *J* = 8.3Hz, 2H), 8.86 (s, 2H), 8.72 (d, *J* = 8.2 Hz, 2H), 7.74-7.60 (m, 4H), 7.56-7.60 (m, 4H), 7.56-7.45 (m, 6H), 4.27 (t, *J* = 7.5Hz, 4H) 1.80 (quin, *J* = 7.5Hz, 4H), 1.55-1.42 (m, 4H), 1.05 (t, *J* = 7.4Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 163.32, 162.99, 137.52, 134.22, 134.01, 131.90, 130.48, 129.73, 128.88, 127.68, 127.58, 127.50, 123.07, 122.18, 122.16, 120.20, 98.54, 90.73, 40.47, 30.21, 20.38, 13.87.

Ranges of Pt-P and Pt-C bond lengths in platinum-diacetylide diphosphine complexes.

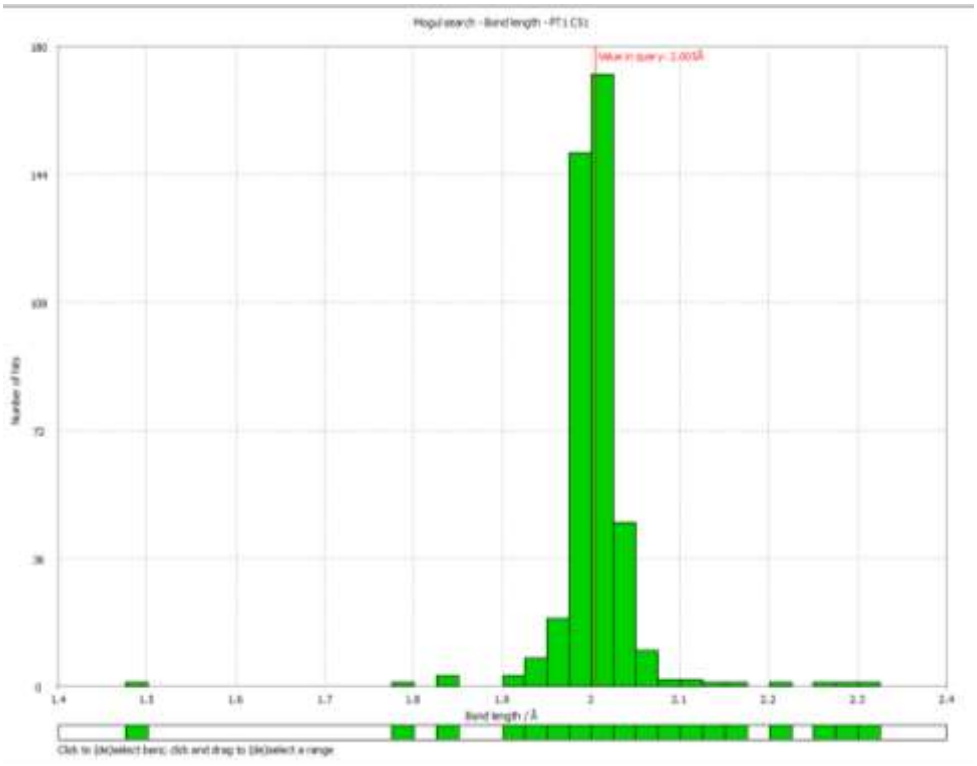


Figure S5. Pt-C bond lengths observed in platinum-diacetylide diphosphine complexes. The corresponding bond length observed in **1** is highlighted by a red line.

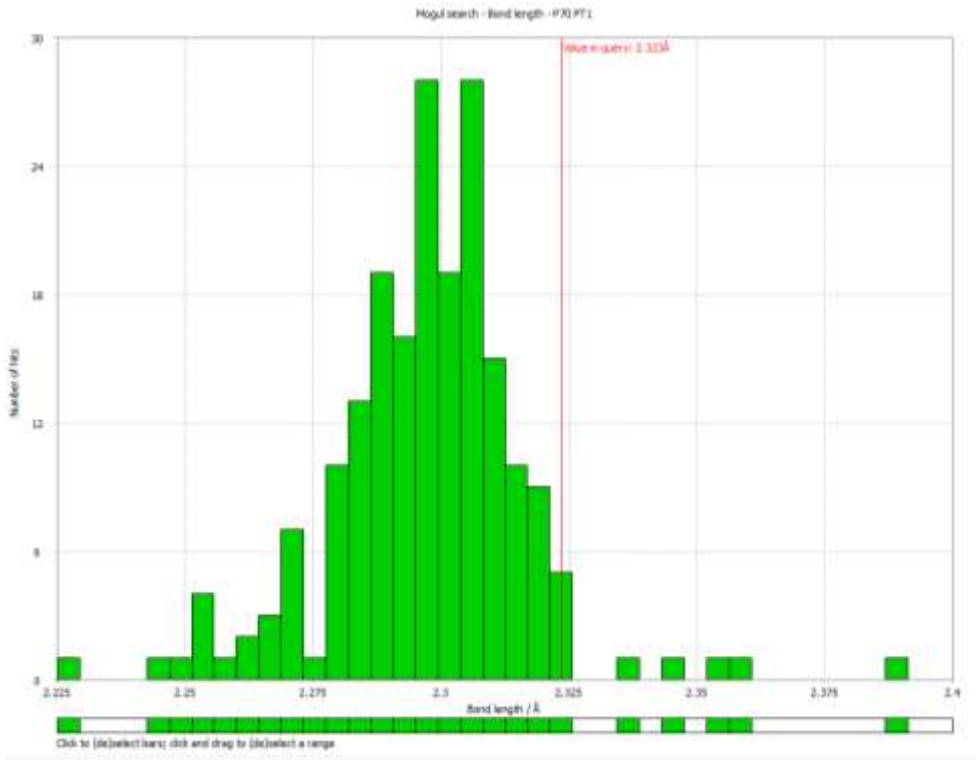


Figure S6. Pt-P bond lengths observed in platinum-diacetylide diphosphine complexes. The corresponding bond length observed in **1** is highlighted by a red line.