Electronic Supplementary Information (ESI) for Chemical Communications

Unprecedented Carbon-Carbon Bond Formation Induced by Photoactivation of a Platinum(IV)-Diazido Complex

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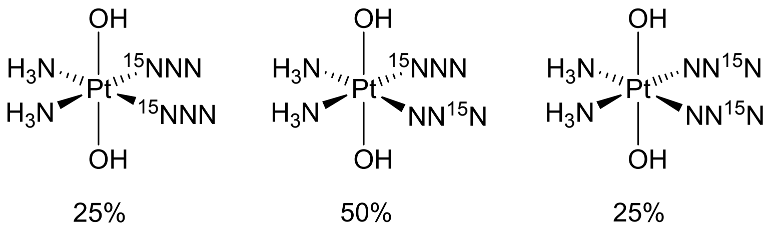
Experimental

Materials. $K_2[PtCl_4]$ was purchased from Precious Metals Online; KI, NaN_3, KOH, NaCl, and HCl from Fisher Scientific; $AgNO_3$, $^{15}NH_4Cl$, $Na(^{15}NN_2)$ (mono-^{15}N-labelled at one *N*-terminus), dimethyl sulfide, and D_2O from Sigma-Aldrich; H_2O_2 (30%) from Polabo; and $HClO_4$ from Fisons.

Complexes *cis*,*trans*,*cis*-$[Pt(N_3)_2(OH)_2(^{15}NH_3)_2]$ (**^{15}N$_2$-1**) and the corresponding ^{15}N-azido (mono-labelled at the N-terminus) labelled analogue *cis*,*trans*,*cis*-$[Pt(^{15}NN_2)_2(OH)_2(^{15}NH_3)_2]$ (**^{15}N$_4$-1**, see below) were synthesized as previously described (P. Müller, B. Schröder, J. A. Parkinson, N. A. Kratochwil, R. A. Coxall, A. Parkin, S. Parsons and P. J. Sadler, *Angew. Chem. Int. Ed.*, 2003, **42**, 335–339). For **^{15}N$_2$-1** $^{15}NH_4Cl$ was used as the source of ^{15}N; for **^{15}N$_4$-1** $^{15}NH_4Cl$ and $Na(^{15}NN_2)$ (mono-^{15}N-labelled at one *N*-terminus) were used as the sources of ^{15}N. Yield: 78-80%. ^{1}H NMR (500.1 MHz, 90% H_2O/10% D_2O, pH 5.4, TSP): δ = 5.12 ppm ($^1J(^{15}N\text{-}H)$ = 73 Hz, $^2J(^{195}Pt\text{-}H)$ = 46 Hz; $Pt^{IV}\text{-}^{15}N\boldsymbol{H}_3$); 2D [^{1}H,^{15}N] HSQC NMR (500.1/50.7 MHz, 90% H_2O/10% D_2O, pH 5.4, $^{15}NH_4Cl$): δ = -40.8 ppm ($^1J(^{195}Pt\text{-}^{15}N)$ = 261 Hz; $Pt^{IV}\text{-}^{15}\boldsymbol{N}H_3$); $^{14}N\{^1H\}$ NMR (36.1 MHz, 90% PBS/10% D_2O, pH 7.4, NH_4Cl): δ = 353.3 (Pt^{IV}-NN***N***), 227.4 (Pt^{IV}-N***N***N), 160.5 (Pt^{IV}-***N***NN), -40.8 ppm ($^1J(^{195}Pt\text{-}^{14}N)$ = 180 Hz; $Pt^{IV}\text{-}\boldsymbol{N}H_3$).



($^{15}N_4$-1)

Warning! *Heavy metal azido complexes are known to be shock-sensitive detonators. We encountered no problems in this study, but these materials should be handled with extreme caution, especially not to put pressure on them in the crystalline form.*

Methods and Instrumentation

NMR Spectroscopy. All NMR spectra were acquired in 90% H_2O/10% D_2O at 298 K on a Bruker DMX500 spectrometer using a TBI [^{1}H,^{13}C,X] probe-head equipped with *z*-field gradients, and on a Bruker Avance 600 spectrometer using a TXI [^{1}H,^{13}C,^{15}N] cryoprobe-head equipped with *z*-field gradients. Data processing was carried out using XWIN-NMR version 2.0 (Bruker U.K. Ltd.) and MestReC version 4.9.9.9 (Mestrelab Research S.L.).

Typical acquisition parameters for 1D ^{1}H NMR spectra (^{1}H: 500.13 MHz): 16 transients, spectral width 7.5 kHz, using 32k data points and a delay time of 2.0 s. Water suppression was achieved using a 55.0 dB power level presaturation. Spectra were processed using exponential weighting with a resolution of 0.5 Hz and a line-broadening threshold of 0.1 Hz. ^{1}H chemical shifts were referenced to TSP (sodium 3-(trimethylsilyl)-[2,2,3,3-D_4]-propionate) *via* internal 1,4-dioxane at 3.764 ppm.

Typical acquisition parameters for 1D ^{14}N{^{1}H} NMR spectra (^{14}N: 36.13 MHz): 64k transients, spectral width 20 kHz, using 32k data points and a delay time of 0.25 s. Sequences were optimized for $^1J(^{14}\text{N-H}) = 60$ Hz, and ^{1}H decoupling was achieved using WALTZ16 pulse sequence. Spectra were processed using exponential weighting with a resolution of 0.6 Hz and a line-broadening threshold of 10 Hz. ^{14}N chemical shifts were referenced to external NH_4Cl 1.5 M in 1 M HCl at 0.00 ppm.

Typical acquisition parameters for 2D [^{1}H,^{13}C] HMBC NMR spectra (^{1}H: 599.92/^{13}C: 150.87 MHz): 1k transients of 32 scans/block, spectral width 6.0/37.7 kHz, using 2k/2k data points and a delay time of 1.5 s. Sequences were optimized for $^1J(^{13}\text{C-H}) = 145$ Hz/$^nJ(^{13}\text{C-H}) = 8$ Hz, and ^{1}H decoupling was achieved using WALTZ16 pulse sequence. Water suppression was achieved using a 47.0 dB power level presaturation. Spectra were processed using cosine-squared weighting with a resolution of 5.9/36.8 Hz and a line-broadening threshold of 0.7/1.0 Hz. ^{1}H chemical shifts were referenced to TSP (sodium 3-

(trimethylsilyl)-[2,2,3,3-D_4]-propionate) *via* internal 1,4-dioxane at 3.764 ppm. ^{13}C chemical shifts were referenced to TMS (tetramethylsilane) *via* internal 1,4-dioxane at 67.19 ppm.

Typical acquisition parameters for 2D [^{1}H,^{15}N] HSQC NMR spectra (^{1}H: 500.13/^{15}N: 50.70 MHz): 512 transients of 16 scans/block, spectral width 7.5/4.6 kHz, using 2k/2k data points and a delay time of 1.5 s. Sequences were optimized for $^1J(^{15}\mathrm{N}\text{-}\mathrm{H})$ = 76 Hz, and ^{1}H decoupling was achieved using WALTZ16 pulse sequence. Spectra were processed using cosine-squared weighting with a resolution of 2.2/3.7 Hz and a line-broadening threshold of 0.7/1.0 Hz. ^{1}H chemical shifts were referenced to TSP (sodium 3-(trimethylsilyl)-[2,2,3,3-D_4]-propionate) *via* internal 1,4-dioxane at 3.764 ppm. ^{15}N chemical shifts were referenced to external $^{15}NH_4Cl$ 1.5 M in 1 M HCl at 0.00 ppm.

Typical acquisition parameters for 2D [^{1}H,^{15}N] HMBC NMR spectra (^{1}H: 599.92/^{15}N: 60.79 MHz): 512 transients of 32 scans/block, spectral width 6.0/6.1 kHz, using 2k/2k data points and a delay time of 1.5 s. Sequences were optimized for $^1J(^{15}\mathrm{N}\text{-}\mathrm{H})$ = 76 Hz/$^nJ(^{15}\mathrm{N}\text{-}\mathrm{H})$ = 4 Hz, and ^{1}H decoupling was achieved using WALTZ16 pulse sequence. Water suppression was achieved using a 47.0 dB power level presaturation. Spectra were processed using cosine-squared weighting with a resolution of 2.9/6.2 Hz and a line-broadening threshold of 0.7/1.0 Hz. ^{1}H chemical shifts were referenced to TSP (sodium 3-(trimethylsilyl)-[2,2,3,3-D_4]-propionate) *via* internal 1,4-dioxane at 3.764 ppm. ^{15}N chemical shifts were referenced to external $^{15}NH_4Cl$ 1.5 M in 1 M HCl at 0.00 ppm.

pH Measurement. pH values were measured at room temperature directly in the NMR tube with a Corning 145 pH-meter equipped with an Aldrich microcombination electrode, calibrated with standard Aldrich buffer solutions at pH 4, 7 and 10.

Mass Spectrometry (ESI-MS). Positive ion electrospray mass spectra were obtained on a Micromass Platform II mass spectrometer. Samples (100 μL) were injected directly into the source by a syringe pump at a flow rate of 0.5 mL h^{-1}, and the ions were produced in an atmospheric pressure ionization (API) ESI ion source. The source temperature was 383 K, and the drying gas (N_2) flow rate was 300 L h^{-1}. A potential of 3.5 kV (capillary voltage) was applied to the probe tip (HV lens voltage: 0.5 kV; multiplier: 650 V), and the cone voltage was + 15 V. Mass spectra were recorded over the scan range 200-800 Da at a scan time rate of 2 s and a resolution of 15 *m/z*. Data acquisition and processing were carried out using MassLynx Software version 3.5 (Waters Corp.).

Photoreactions. Samples for the photochemical studies were 10-13 mM solutions of the investigated Pt^{IV} complexes in 0.6 mL 90% H_2O/10% D_2O; pH values were adjusted before irradiation using dilute $HClO_4$ solutions. Before irradiation, the samples were transferred into 5 mm screw-cap NMR tubes (Wilmad) provided with a teflon/silicone septum, and Ar was bubbled into the solutions for 30 min. Soon after Ar saturation, NMR samples were irradiated at for 2 h at 310 K using a LZC-ICH2 photoreactor

(Luzchem) equipped with a temperature controller and 14 LZC-UVA lamps (Hitachi, $\lambda_{max} = 365.0$ nm) with no other sources of light filtration. The power levels ($P = 6.4\text{-}7.2$ mW cm^{-2}) were monitored and assessed using the appropriate probe window, calibrated against an OAI-306 UV power meter from Optical Associates, Inc.; the delivered radiation dose (J cm^{-2}) is defined as irradiance (P, W cm^{-2}) × time (s). NMR spectra were then recorded soon after irradiation.

Po_2 Measurement. Po_2 values were measured with a Corning 240 pH-meter (switched to read millivolts) equipped with a Lazar DO-166-NP dissolved oxygen needle probe. Calibration was carried out at 295 K at a barometric pressure of 761 mm Hg using a 0.1 g L^{-1} NaCl solution in double-distilled water (made freshly) reading, in equilibrium with atmospheric dioxygen, a Po_2 value of 161 mm Hg (expected: 163 mm Hg). The pH-meter was then set up to read Po_2 directly in mm of Hg partial pressure.

SO_4^{2-} Qualitative Detection. A sample containing **$^{15}N_4$-1** (10.9 mM) in presence of DMS (68.2 mM; mol ratio = 1:6.2) in 90% H_2O/10% D_2O (Ar-saturated, initial pH 4.9) was irradiated for 2 h ($\lambda_{max} = 365.0$ nm, $P = 6.4$ mW cm^{-2}, dose = 49.5 J cm^{-2}, 310 K; final pH 10.4, re-adjusted to 3.2). An aliquot of this solution (100 μL) was acidified with concentrated $HClO_4$ to a final pH < 1, and treated with two drops of a saturated solution of $BaCl_2$. A white precipitate ($BaSO_4$) formed immediately.

Tables

Table S1. ^{1}H/^{15}N chemical shifts, coupling constants and assignments of the peaks produced after 2 h of irradiation (λ_{max} = 365.0 nm, P = 7.2 mW cm^{-2}, dose = 52.0 J cm^{-2}, 310 K) of complex **$^{15}N_2$-1** (12.9 mM in 90% H_2O/10% D_2O, Ar-saturated, pH 5.1 (initial)/10.7 (final; re-adjusted to 3.1)) (see Figure S2). Yields of Pt-ammino species in solution are based on the integrals of the corresponding NMR peaks.

Peak	Chemical shifts (ppm)		Coupling constants (Hz)			Assignment / Yield (%)
	δ(^{1}H)	δ(^{15}N)	^1J(^{15}N-H)	^1J(^{195}Pt-^{15}N)	^2J(^{195}Pt-H)	
2	4.06	-73.0	72	n.d.	n.d.	*t*-($^{15}NH_3$-Pt^{II}-N/O) / 1.9
3	4.04	-69.0	72	280	55	*t*-($^{15}NH_3$-Pt^{II}-N) / 56.4
4	3.90	-67.3	73	n.d.	n.d.	*t*-($^{15}NH_3$-Pt^{II}-N) / 2.6
5	4.09	-65.8	72	n.d.	n.d.	*t*-($^{15}NH_3$-Pt^{II}-N) / 14.7
6	5.80	-53.7	73	258	48	*t*-($^{15}NH_3$-Pt^{IV}-O) / 1.9
7	5.30	-51.4	74	261	48	*t*-($^{15}NH_3$-Pt^{IV}-O) / 16.0
8	5.51	-50.9	73	260	48	*t*-($^{15}NH_3$-Pt^{IV}-O) / 3.9
9	5.46	-42.4	73	265	48	*t*-($^{15}NH_3$-Pt^{IV}-N) / 2.6
10	7.11	-2.2	73	-	-	$^{15}NH_4^+$

Table S2. ^{1}H/^{13}C chemical shifts, coupling constants and assignments of the peaks produced after 2 h of irradiation (λ_{max} = 365.0 nm, P = 6.4 mW cm^{-2}, dose = 49.5 J cm^{-2}, 310 K) of complex **$^{15}N_4$-1** (10.9 mM) in presence of DMS (68.2 mM; molar ratio 1:6.2) in 90% H_2O/10% D_2O (Ar-saturated, pH 4.9 (initial)/10.4 (final)) (see Figure 1 and Figure S3).

Peak	Chemical shifts (ppm)		Coupling constants (Hz)		Assignment
	$\delta(^{1}H)$	$\delta(^{13}C)$	$^{3}J(^{1}H-^{1}H)$	$^{1}J(^{13}C-H)$	
α	1.19	17.4	7	129	CH_3-C-
β	3.66	58.2	7	147	C-CH_2-
γ	3.36	44.7	-	139	$DMSO_2$
δ	2.73	39.4	-	141	DMSO
ε	2.11	17.2	-	141	DMS
ζ	1.92	6.5	-	140	n.a.

Table S3. $^1H/^{15}N$ chemical shifts, coupling constants and assignments of the peaks produced after 2 h of irradiation (λ_{max} = 365.0 nm, P = 6.4 mW cm^{-2}, dose = 49.5 J cm^{-2}, 310 K) of complex $\mathbf{^{15}N_4}$**-1** (10.9 mM) in presence of DMS (68.2 mM; molar ratio 1:6.2) in 90% H_2O/10% D_2O (Ar-saturated, pH 4.9 (initial)/10.4 (final; re-adjusted to 3.2)). Yields of Pt-ammino species in solution are based on the integrals of the corresponding NMR peaks.

Chemical shifts (ppm)		Coupling constants (Hz)			Assignment / Yield (%)
$\delta(^1H)$	$\delta(^{15}N)$	$^1J(^{15}N\text{-}H)$	$^1J(^{195}Pt\text{-}^{15}N)$	$^2J(^{195}Pt\text{-}H)$	
4.02	-69.0	72	284	55	t-($^{15}NH_3$-Pt^{II}-N) / 12.6
3.81	-68.1	70	282	55	t-($^{15}NH_3$-Pt^{II}-N) / 4.4
4.07	-65.6	72	289	53	t-($^{15}NH_3$-Pt^{II}-N) / 8.9
3.65	-64.5	91	n.d.	n.d.	CH_3CH_2-^{15}NH-Pt^{II} / 63.3
5.69	-54.4	73	261	48	t-($^{15}NH_3$-Pt^{IV}-O) / 1.9
5.24	-51.2	70	259	47	t-($^{15}NH_3$-Pt^{IV}-O) / 7.6
5.39	-42.6	73	267	48	t-($^{15}NH_3$-Pt^{IV}-N) / 1.3
7.11	-2.2	73	-	-	$^{15}NH_4^+$

Figures

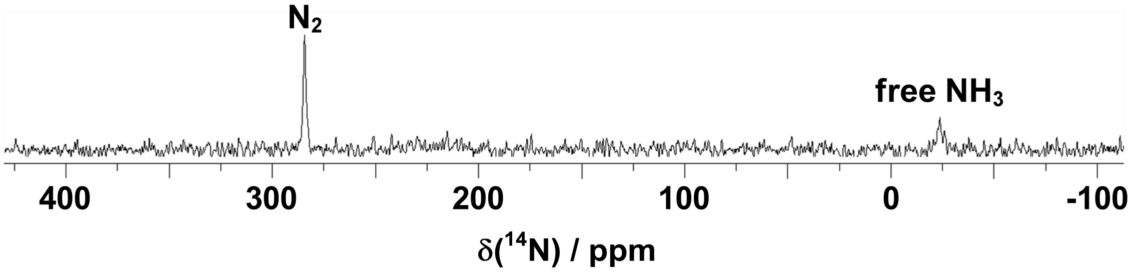


Figure S1. 1D $^{14}N\{^1H\}$ NMR spectrum of **$^{15}N_2$-1** (12.9 mM in 90% H_2O/10% D_2O, Ar-saturated, initial pH 5.1) after 2 h of irradiation (λ_{max} = 365.0 nm, P = 7.2 mW cm^{-2}, dose = 52.0 J cm^{-2}, 310 K; final pH 10.7).

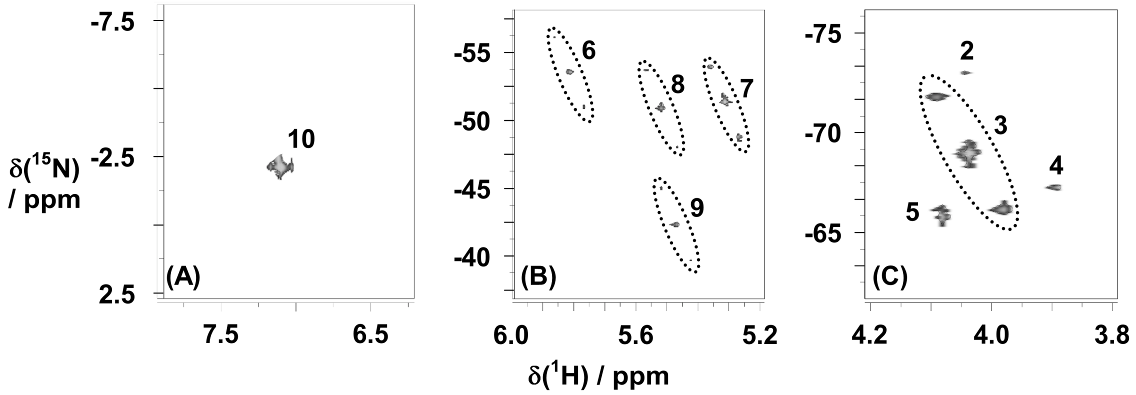


Figure S2. 2D [^{1}H,^{15}N] HSQC NMR spectrum of **^{15}N$_2$-1** (12.9 mM in 90% H_2O/10% D_2O, Ar-saturated, initial pH 5.1) after 2 h of irradiation (λ_{max} = 365.0 nm, P = 7.2 mW cm^{-2}, dose = 52.0 J cm^{-2}, 310 K; final pH 10.7), and pH adjustment to 3.1: (A) NH_4^+, (B) Pt^{IV}-NH_3, and (C) Pt^{II}-NH_3 spectral regions (see Table S1).

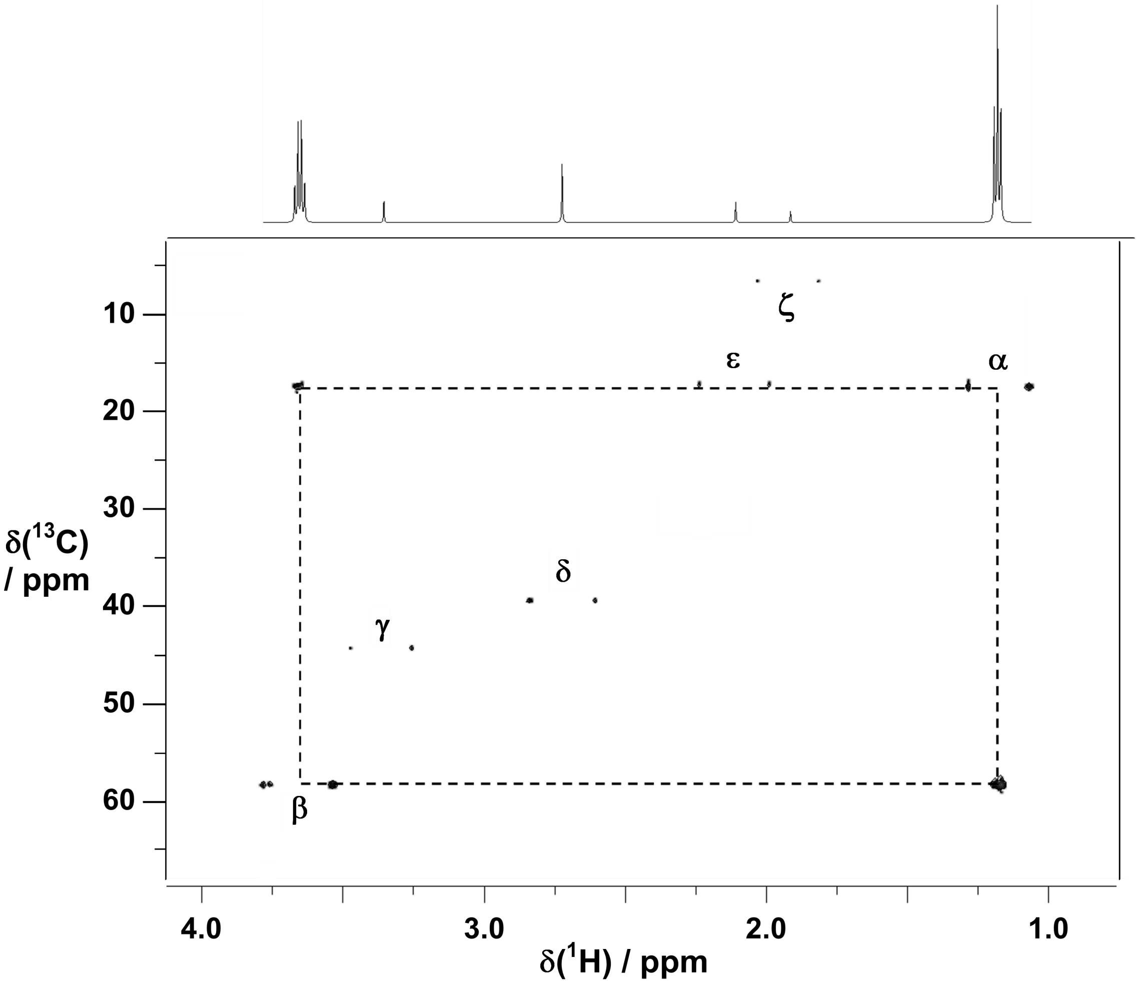


Figure S3. 2D [^{1}H,^{13}C] HMBC NMR spectrum of complex $\mathbf{^{15}N_4\text{-}1}$ (10.9 mM) in presence of DMS (68.2 mM; mol ratio 1:6.2) in 90% H_2O/10% D_2O (Ar-saturated, initial pH 4.9) after 2 h of irradiation (λ_{max} = 365.0 nm, P = 6.4 mW cm^{-2}, dose = 49.5 J cm^{-2}, 310 K; final pH 10.4) (see Figure 1 and Table S2).

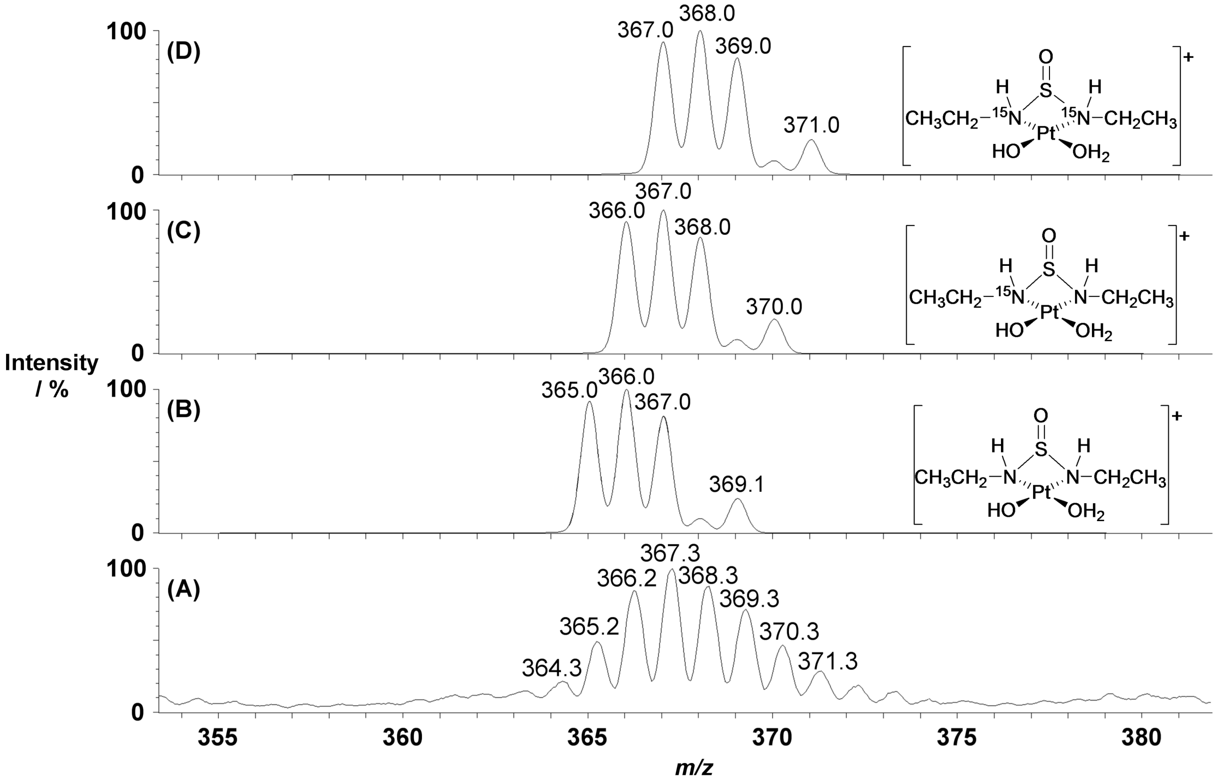


Figure S4. (A) Part of the ESI mass spectrum in positive ion mode (cone voltage: +15 V) of a sample containing ^{15}**N$_4$-1** (10.9 mM) in presence of DMS (68.2 mM; mol ratio = 1:6.2) in 90% H_2O/10% D_2O (Ar-saturated, initial pH 4.9) after 2 h of irradiation (λ_{max} = 365.0 nm, P = 6.4 mW cm^{-2}, dose = 49.5 J cm^{-2}, 310 K; final pH 10.4, re-adjusted to 3.2), and isotope models for (B) $C_4H_{15}N_2O_3PtS$, (C) $C_4H_{15}{}^{15}NNO_3PtS$, and (D) $C_4H_{15}{}^{15}N_2O_3PtS$.