Supporting Information for:

Modulating Sterics in Trimethyl Platinum (IV) Diimine Complexes to Achieve C-C Bond-Forming Reductive Elimination

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I. General Experimental

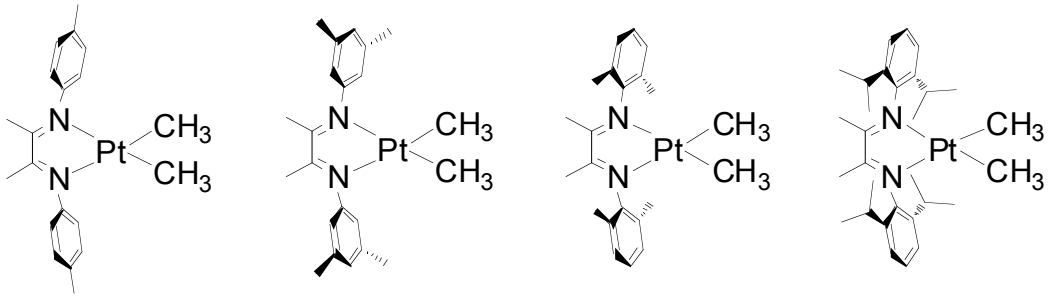
All solutions were prepared in a nitrogen (N_2) filled glove-box unless otherwise noted. All reagents were purchased from Aldrich® and stored directly for use in an N_2 filled glove-box unless noted. Silver hexafluorophosphate ($AgPF_6$) was stored at –35 °C in the glove box freezer. Acetonitrile was purchased from Burdick and Jackson® (low-water brand) and stored in an argon pressurized stainless steel drum plumbed directly into a glove-box. All other solvents were purchased from Fisher Scientific with the exception of deuterated solvents, which were purchased from Cambridge Isotope Laboratories. Acetone, acetone-d_6, nitromethane-d_3, and iodomethane (MeI) were purified by vacuum distillation twice from $CaSO_4$. Dichloromethane-d_2 was purified by vacuum distillation from CaH_2. Diethyl ether, benzene, pentane, and toluene were dried using a Seca Solvent System installed by GlassContour.[1] Pentane, toluene, and diethyl ether were further purified by vacuum distillation from Na^0 and benzophenone. Sodium iodide (NaI), was dried under vacuum for 12 h at 80 ºC.

J. Young NMR tubes were purchased from Chemglass®. Hamilton gas-tight syringes (volumes between 10 μL and 1 mL) were used for preparing solutions of accurate volumes. ^{1}H NMR spectra were obtained on Bruker AV301, DRX499, AV500, or Varian Inova 400, 500 or MR400 spectrometers and ^{1}H NMR data were processed using VNMRJ 2.2, Topspin 2.1 or MestReC©. Chemical shifts were reported relative to TMS by referencing the residual solvent. Hexamethyldisiloxane (HMDS) and 1,1,2-trichloroethane (TCE) were used as internal integration standards. Due to the long T_1 time of ethane, yields were determined using NMR spectra that were collected with a delay of at least 180s. The error in the ^{1}H NMR yields were estimated as 4-9% based on ^{1}H NMR integration. The errors in the rate constants and activation barriers were determined based on the error of the fit and the standard deviation of repeated measurements where

indicated. DFT calculated geometries were displayed visually using ChemCraft ver. 1.5.

II. Syntheses

$(DAB)Pt^{II}(CH_3)_2$ complexes,[2] **1A-D** (**Figure S1**), and silver tetrakis(pentafluorophenyl)borate[3] were synthesized following previous published procedures. Acylferrocenium hexafluorophosphate ($AcFcPF_6$) was prepared as described for acylferrocenium tetrafluoroborate ($AcFcBF_4$)[4] by substituting silver tetrafluoroborate with silver hexafluorophosphate.



$(DAB_A)Pt(CH_3)_2$ (**1A**) $(DAB_B)Pt(CH_3)_2$ (**1B**) $(DAB_C)Pt(CH_3)_2$ (**1C**) $(DAB_D)Pt(CH_3)_2$ (**1D**)

Figure S1. $(DAB)Pt^{II}(CH_3)_2$ complexes, **1A-D**.

III. Analyses of Ethane Generation from $(DAB)Pt^{II}(CH_3)_2$ complexes.

In general, reaction solutions were prepared in a nitrogen filled glove-box at room temperature. Solutions containing the $(DAB)Pt^{II}(CH_3)_2$ complexes and the internal standard (HMDS or TCE) were added to J. Young NMR tubes and an NMR spectrum was obtained to determine initial integration vs. the standard. With the NMR tube back inside the glove-box, solutions of MeI, $AgPF_6$ or $AcFcBF_4$ were prepared and added to the solutions of **1**. After each addition, the NMR tubes were immediately sealed and inverted at least 5 times to ensure proper mixing. ^1H NMR data for the new tri-methyl Pt^{IV} iodo complexes, $(DAB_X)Pt^{IV}(CH_3)_3I$ (**2X-I**)[5] (X = ligands A through D)

were consistent with the reported data for the similar complex (bis(*p*-tolylimino)acenaphthene)$Pt^{IV}(CH_3)_3I$.[6] The tri-methyl Pt^{IV} iodo complexes are stable in NMR solutions, but attempts to isolate these complexes in most cases resulted in decomposition. As a result, full characterization of these complexes was not performed. After adding the silver salts, the tubes were centrifuged to force all the AgI to the bottom of the tube. Solutions of the new cationic tri-methyl Pt^{IV} complexes[5] were heated and monitored using NMR spectroscopy to detect ethane (δ 0.83 at 25 °C in acetone-d_6) and the cationic mono-methyl Pt^{II} products as described in the following sections.

Ethane yields were determined from the ^{1}H NMR integrals using the previously described calibration method and calibration curve measured for acetone-d_6.[7] An analogous calibration curve for quantification of ethane in nitromethane-d_3 was generated, **Figure S2**. Ethane was condensed from a calibrated volume bulb into a J. Young valve NMR tube containing a known concentration of TCE in nitromethane-d_3. The concentrations of ethane in each tube were determined by ^{1}H NMR using a delay time of 180 s. In a few cases, ethane yields in other solvents were estimated with the assumption that the acetone calibration curve could be used.

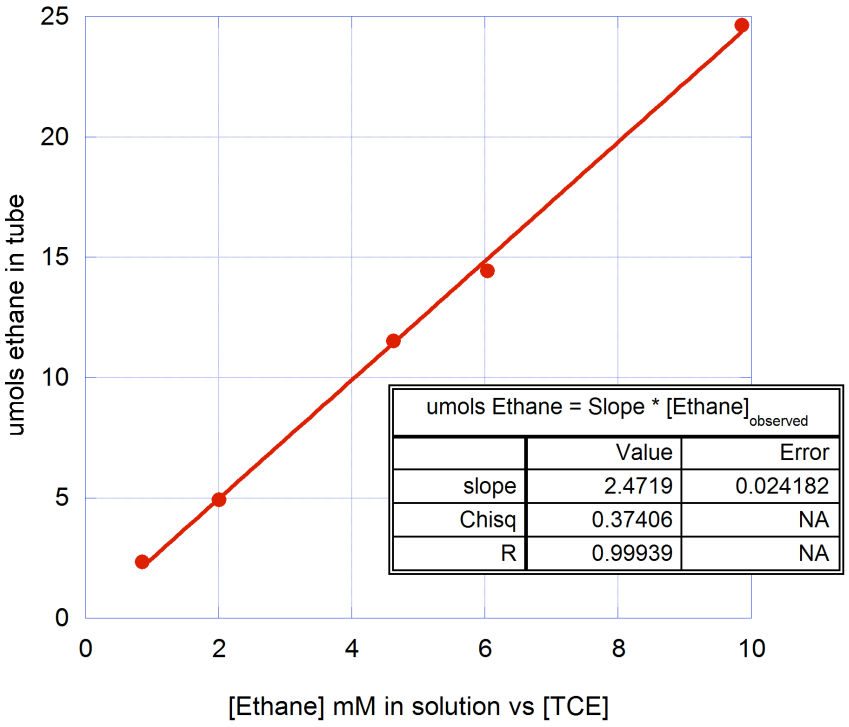


Figure S2. Calibration curve for ethane quantification in CD_3NO_2.

IV. Reactions

A. $(DAB_A)Pt^{II}(Me)_2$ (1A).

Reactions in acetone-d_6. Treating a solution of **1A** (2.5 μmol) with 1.05 equiv. of MeI in acetone-d_6 produced a yellow solution within 1 min. at 25 ºC. By ^{1}H NMR, new peaks consistent with a tri-methyl Pt complex, $(DAB_A)Pt^{IV}(CH_3)_3I$ (**2A-I**), were observed as the major product in 99% yield (**Figure S3**). ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $(DAB_A)Pt^{IV}(CH_3)_3I$ δ 0.66 (3H, s, $^2J_{195Pt-H}$ = 73.0 Hz, PtC$H_{3,ax}$), 0.80 (6H, s, $^2J_{195Pt-H}$ = 72.0 Hz, PtC$H_{3,eq}$), 2.40 (6H, s, ArCH_3), 2.45 (6H, s, CCH_3), 6.82 (2H, broad s, Ar*H*), 7.33 (2H, s, Ar*H*), 7.35 (2H, s, Ar*H*), 7.56 (2H, broad s, Ar*H*).

An acetone-d_6 solution of $AgPF_6$ (1.05 equiv.) was added to **2A-I** inside of the glove box. The resulting solution was analyzed by ^{1}H NMR revealing a new spectrum consistent with the cationic tri-methyl Pt^{IV} complex, $[(DAB_A)Pt^{IV}(CH_3)_3(solv)]^+$, **2A**. ^{1}H NMR (400 MHz, 25 ºC, acetone-d_6): $[(DAB_D)Pt^{IV}(CH_3)_3(solv)]^+$ δ 0.68 (6H, s, $^2J_{195Pt-H}$ = 67.2 Hz, PtC$H_{3,eq}$), 1.06 (3H, s, $^2J_{195Pt-H}$ = 82.4 Hz, PtC$H_{3,ax}$), 2.42 (6H, s, ArCH_3), 2.50 (6H, s, CCH_3), 6.97 (4H, d, $^3J_{H-H}$ = 8.4 Hz, Ar*H*), 7.41 (4H, d, $^3J_{H-H}$ = 8.4 Hz, Ar*H*).

Solutions of **2A** were heated to 60 °C and monitored by ^{1}H NMR, **Figure S2**. After 24 h of heating, a new set of resonances, which also correspond to a trimethyl Pt^{IV} complex $(DAB_A)Pt^{IV}(CH_3)_3X$ was observed in 85% yield relative to **1A** (here X denotes an unknown axial ligand). No ethane was observed over the course of this reaction. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $(DAB_A)Pt^{IV}(CH_3)_3X$ δ 0.59 (6H, s, $^2J_{195Pt-H}$ = 67.6 Hz, PtC$H_{3,eq}$), 0.65 (3H, s, $^2J_{195Pt-H}$ = 84.0 Hz, PtC$H_{3,ax}$), 2.41 (12H, s, ArCH_3 and CCH_3), 6.99 (4H, multiple peaks, Ar*H*), 7.38 (4H, multiple peaks, Ar*H*).

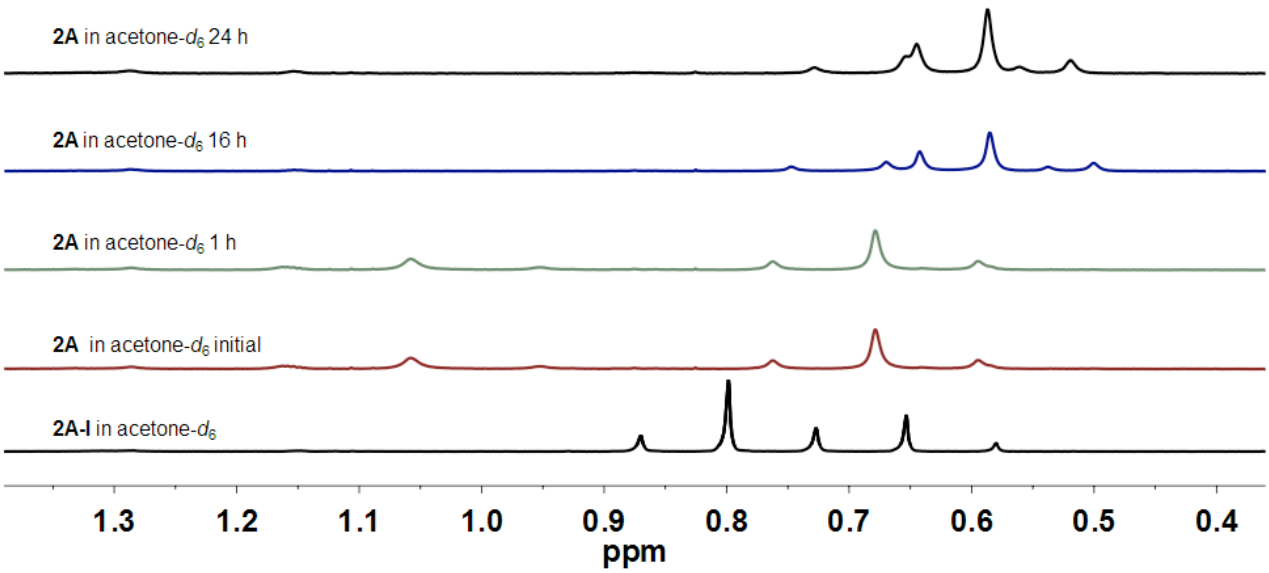


Figure S3. ^{1}H NMR spectra showing conversion of $(DAB_A)Pt^{IV}(CH_3)_3I$ (**2A-I**) to $[(DAB_A)Pt^{IV}(CH_3)_3(solv)]^+$ (**2A**) and subsequent thermolysis of **2A** in acetone-d_6 at 60 °C. Truncated to show the Pt–CH_3 region of the spectra.

Reactions in nitromethane-d_3. Treating a solution of **1A** (2.5 μmol) with 1.05 equiv. of MeI in nitromethane-d_3 produced a yellow solution within 1 min. at 25 ºC. Addition of a nitromethane-d_3 solution of $AgPF_6$ (1.1 equiv.) was immediately performed inside of the glove box and the solution was analyzed by ^{1}H NMR to reveal a new spectrum that is consistent with the cationic tri-methyl Pt^{IV} complex, $[(DAB_A)Pt^{IV}(CH_3)_3]^+$, **2A (Figure S4)**. All of the ^{1}H NMR peaks were significantly broadened. ^{1}H NMR (400 MHz, 25 ºC, nitromethane-d_3): $[(DAB_A)Pt^{IV}(CH_3)_3]^+$ δ 0.98-46 (9H, $Pt(CH_{3,})_{2,eq}$ and $PtCH_{3,ax}$), 2.43 (12H, multiple peaks), 6.92-6.90 (4H, Ar*H*), 7.43-7.41 (4H, Ar*H*).

Solutions of **2A** were heated to 60 °C and monitored by ^{1}H NMR, **Figure S4**. After 16 h of heating, **2A** was still present in 91%, and a trace of ethane was observed.

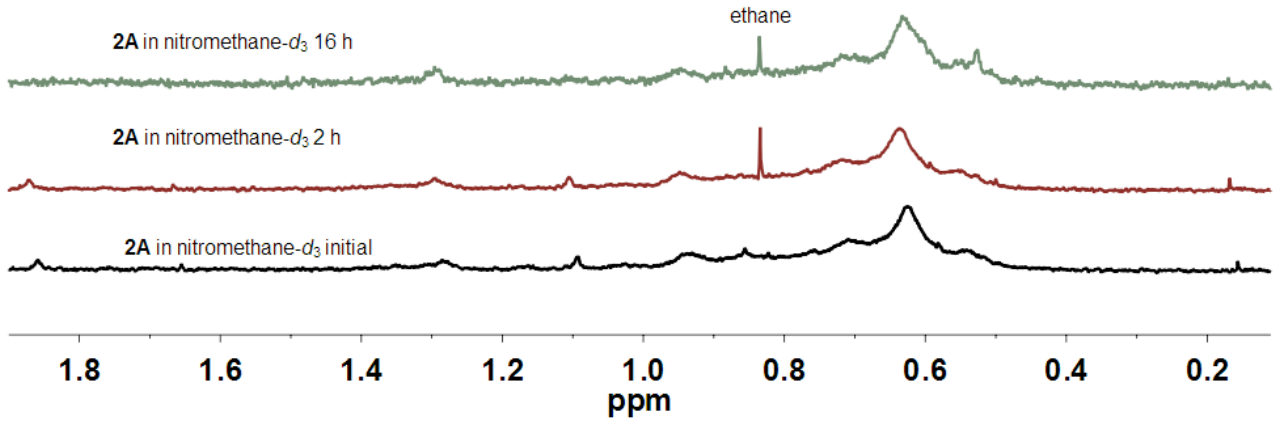


Figure S4. ^{1}H NMR spectra of decomposition of $[(DAB_A)Pt^{IV}(CH_3)_3]$+ (**2A**) in nitromethane-d_3 at 60 °C. Truncated to show the Pt–CH_3 region of the spectra.

Reactions in dichloromethane-d_2. A 3.57 mM solution of **1A** (2.5 μmol) in dichloromethane-d_2 was treated with 3.0 μmol of MeI and the solution turned yellow. Analysis by ^{1}H NMR at 25 °C revealed a new set of peaks analogous to those described above for **2A-I** as the major product in 107 % yield (**Figure S4**). ^{1}H NMR (500 MHz, 25 ºC, dichloromethane-d_2): $(DAB_A)Pt^{IV}(CH_3)_3I$ (**2A-I**) δ 0.68 (3H, s, $^2J_{195Pt-H}$ = 73.5 Hz, PtC$H_{3,ax}$), 0.82 (6H, s, $^2J_{195Pt-H}$ = 71.0 Hz, Pt(CH_3)$_{2,eq}$), 2.30 (6H, s, ArCH_3), 2.42 (6H, s, CCH_3), 6.70 (2H, broad s, Ar*H*), 7.31 (4H, broad s, Ar*H*), 7.51 (2H, broad s, Ar*H*).

A dichloromethane-d_2 solution of $AgPF_6$ (2.0 equiv.) was added inside of the glove box and the solution was analyzed by ^{1}H NMR to reveal a new spectrum consistent with the cationic tri-methyl Pt^{IV} complex, $[(DAB_A)Pt^{IV}(CH_3)_3]^+$, **2A**. ^{1}H NMR (400 MHz, 25 ºC, dichloromethane-d_2): $[(DAB_A)Pt^{IV}(CH_3)_3]^+$ δ 0.91 (9H, broad s, $^2J_{195Pt-H}$ = 67.0 Hz, Pt(CH_3)$_3$), 2.41 (6H, s, ArCH_3), 2.44 (6H, s, CCH_3), 6.86 (4H, d, $^3J_{H-H}$ = 8.4 Hz, Ar*H*), 7.37 (4H, d, $^3J_{H-H}$ = 8.4 Hz, Ar*H*).

Solutions of **2A** were heated to 50 °C and monitored by ^{1}H NMR, **Figure S5**. After 24 h of heating, 65% of **2A** was observed along with ~16% ethane. New, unidentified resonances grew in at 0.47 ppm and 0.30 ppm (not shown in **Figure S5**).

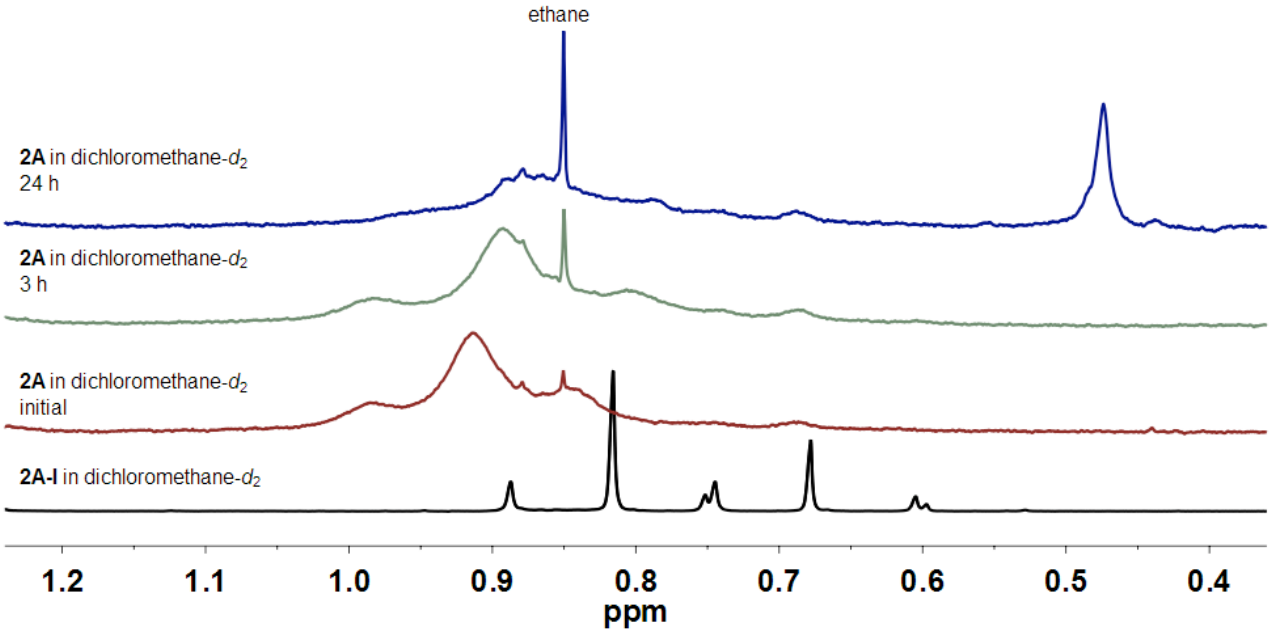


Figure S5. ^{1}H NMR spectra showing conversion of $(DAB_A)Pt^{IV}(CH_3)_3I$ (**2A-I**) to $[(DAB_A)Pt^{IV}(CH_3)_3]+$ (**2A**) and subsequent thermolysis of **2A** in dichloromethane-d_2 at 50 °C. Truncated to show the Pt–CH_3 region of the spectra.

B. $(DAB_B)Pt^{II}(Me)_2$ (1B).

Reactions in acetone-d_6. Treating a solution of **1B** (3.9 μmol) with 1.05 equiv. of MeI in acetone-d_6 produced a pale yellow-green solution after 15 min. at 25 ºC. Analysis by ^{1}H NMR at 25 °C revealed a set of peaks that were consistent with oxidative addition to make an iodide bound complex, $(DAB_B)Pt^{IV}(CH_3)_3I$, **2B-I**, **Figure S6**. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $(DAB_B)Pt^{IV}(CH_3)_3I$ δ 0.66 (3H, s, $^2J_{195Pt-H}$ = 73.4 Hz, PtC$H_{3,ax}$), 0.82 (6H, s, $^2J_{195Pt-H}$ = 71.8 Hz,

Pt(CH_3)$_{2,eq}$), 2.35 (12H, s, ArCH_3), 2.43 (6H, s, CCH_3), 6.54 (2H, s, Ar*H*), 7.00 (2H, s, Ar*H*), 7.34 (2H, s, Ar*H*).

$AgPF_6$ (1.05 equiv.) was added inside of the glove box to produce a light yellow solution with a green precipitate. The ^{1}H NMR spectrum revealed a new product with a pattern consistent with [(DAB$_B$)Pt^{IV}(CH$_3$)$_3$(solv)]$^+$, **2B**. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): [(DAB$_B$)Pt^{IV}(CH$_3$)$_3$]$^+$ δ 0.68 (6H, s, $^2J_{195Pt-H}$ = 66.7 Hz, Pt(CH_3)$_{2,eq}$), 1.06 (3H, s, $^2J_{195Pt-H}$ = 83.3 Hz, PtC$H_{3,ax}$), 2.37 (12H, broad s, ArCH_3), 2.49 (6H, s, CCH_3), 6.69 (4H, s, Ar*H*), 7.08 (2H, s, Ar*H*).

After 16 hours at 25 ºC, solutions of **2B** were heated to 50 °C and monitored by ^{1}H NMR spectroscopy over time. After 48 hours at 50ºC, the peaks identified for [(DAB$_B$)Pt^{IV}(CH$_3$)$_3$]$^+$ above slowly decrease in intensity as a new set of peaks, which also correspond to a tri-methyl Pt^{IV} complex ([(DAB$_B$)Pt^{IV}(CH$_3$)$_3$(X)]$^+$), is formed. Importantly, no ethane is observed. X in this case represents an unknown ligand that is occupying the sixth coordination site of Pt. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): [(DAB$_B$)Pt^{IV}(CH$_3$)$_3$(X)]$^+$ δ 0.59 (6H, s, $^2J_{195Pt-H}$ = 67.7 Hz, Pt(CH_3)$_{2,eq}$), 0.63 (3H, s, $^2J_{195Pt-H}$ = 83.5 Hz, PtC$H_{3,ax}$), 2.36 (12H, s, ArCH_3), 2.39 (6H, s, CCH_3), 6.57 (2H, broad s, Ar*H*), 6.87 (2H, broad s, Ar*H*), 7.02 (2H, s, Ar*H*).

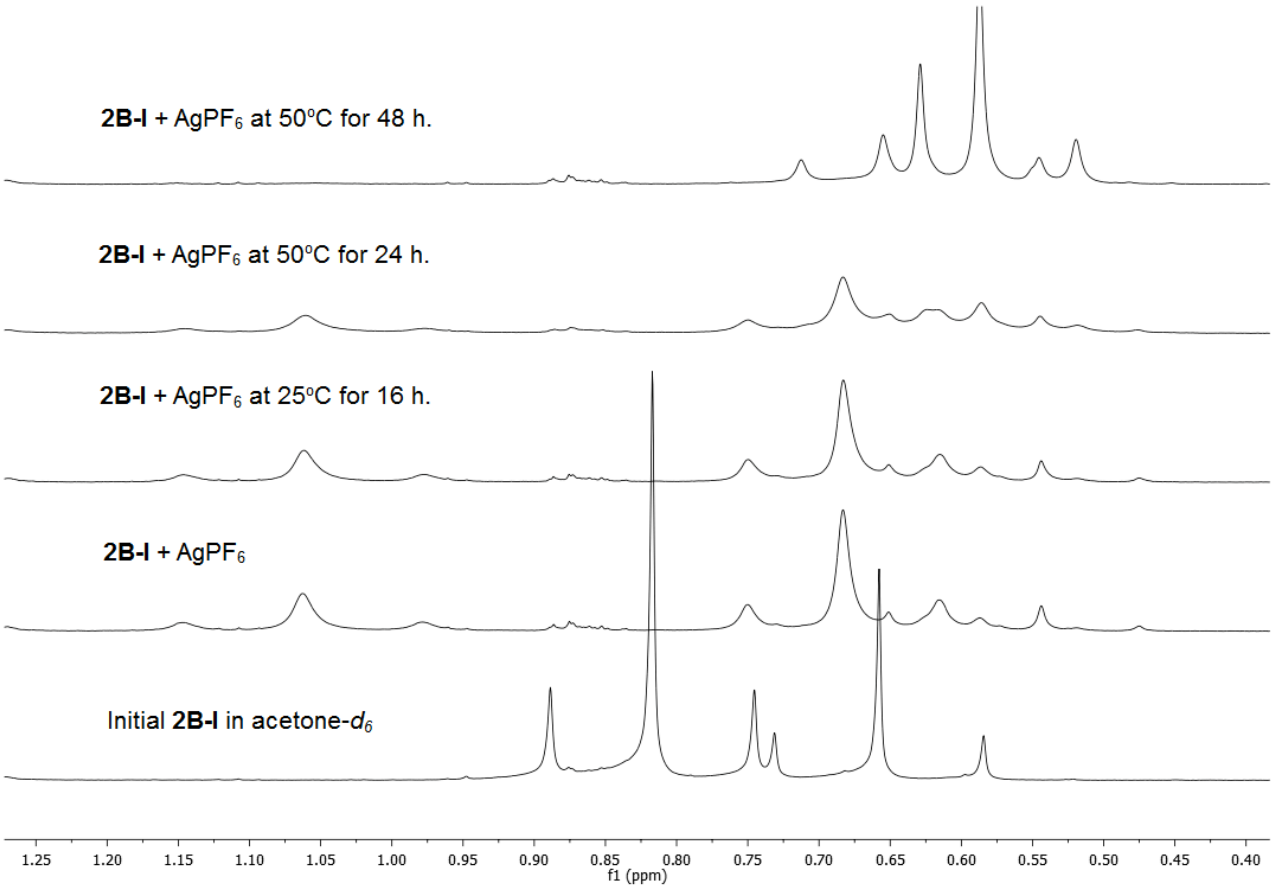


Figure S6. ^{1}H NMR spectra of the reaction between $(DAB_B)Pt^{IV}(CH_3)_3I$ (**2B-I**) and $AgPF_6$ in acetone-d_6 at 50 °C. Truncated to show the Pt-CH_3 region of the spectra.

Reactions in nitromethane-d_3. 2.0 mg of **1B** (3.9 μmol) was treated with 0.60 mL of nitromethane-d_3 and 1.05 equiv of MeI. **1B** is minimally soluble in nitromethane-d_3. A pale yellow-green solution was produced after 15 min. at 25 ºC. Analysis by ^{1}H NMR at 25 °C revealed a set of peaks that were consistent with oxidative addition to make an iodide bound complex, $(DAB_B)Pt^{IV}(CH_3)_3I$, **2B-I**. ^{1}H NMR (500 MHz, 25 ºC, nitromethane-d_3): $(DAB_B)Pt^{IV}(CH_3)_3I$ δ 0.71 (3H, s, $^{2}J_{195Pt\text{-}H}$ = 73.8 Hz, PtC$H_{3,ax}$), 0.75 (6H, s, $^{2}J_{195Pt\text{-}H}$ = 70.9 Hz, Pt(CH_3)$_{2,eq}$), 2.39 (18H, broad asymmetric s, CCH_3 and ArCH_3), 6.57 (2H, s, Ar*H*), 7.03 (2H, s, Ar*H*), 7.24 (2H, s, Ar*H*).

Addition of $AgPF_6$ (1.05 equiv.) inside of the glove box produced a light yellow solution with a green precipitate. The ^{1}H NMR spectrum revealed a new product with a pattern consistent with $[(DAB_B)Pt^{IV}(CH_3)_3]^+$, **2B**. ^{1}H NMR (500 MHz, 25 ºC, nitromethane-d_3): $[(DAB_B)Pt^{IV}(CH_3)_3]^+$ δ 0.62 (6H, s, $^2J_{195Pt\text{-}H}$ = 67.0 Hz, $PtCH_{3,eq}$), 0.93 (3H, s, $^2J_{195Pt\text{-}H}$ = 78.5 Hz, $Pt(CH_3)_{2,ax}$), and several unidentifiable broad signals centered about δ 2.36 and 6.62. After 16 hours at 25 ºC, solutions of **2B** were heated to 50 °C and monitored by ^{1}H NMR spectroscopy over time. No ethane and very little change in the spectra were observed, **Figure S7**.

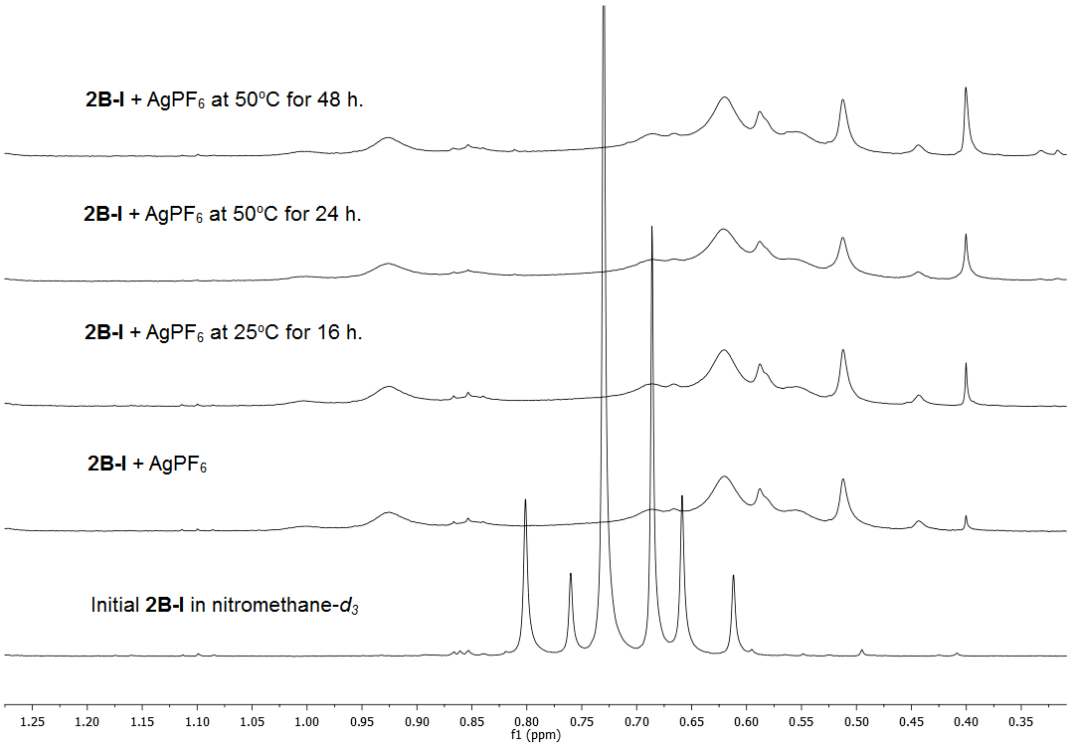


Figure S7. ^{1}H NMR spectra of the reaction between $(DAB_B)Pt^{IV}(CH_3)_3I$ (**2B-I**) and $AgPF_6$ in nitromethane-d_3 at 50 °C. Truncated to show the Pt–CH_3 region of the spectra.

In addition to inhibition of reductive-elimination of ethane being caused by solvent coordination, the possibility of counterion coordination was investigated by changing anion from PF_6^- to the less coordinating counterion, $B(C_6F_5)_4^-$. 1.3 mg of **1B** (2.5 μmol) was treated with 1.35 ml of

nitromethane-d_3 and 1.1 equiv of MeI. The solution turned to a pale yellow-green color and 0.6 ml was added to a J Young NMR tube. Analysis by ^{1}H NMR at 25 °C revealed a set of peaks that were consistent with oxidative addition to make the iodide bound complex, $(DAB_B)Pt^{IV}(CH_3)_3I$, **2B-I**. 1.05 equiv of $AgB(C_6F_5)_4$•$2Et_2O$ was added to generate a new spectrum consisting of broad peaks that were not identified, **Figure S8**. Heating this solution to 60 °C for 24 h. did not generate ethane. After adding NaI, the ^{1}H NMR spectrum showed that **2B-I** was regenerated without forming any other significant by-products.

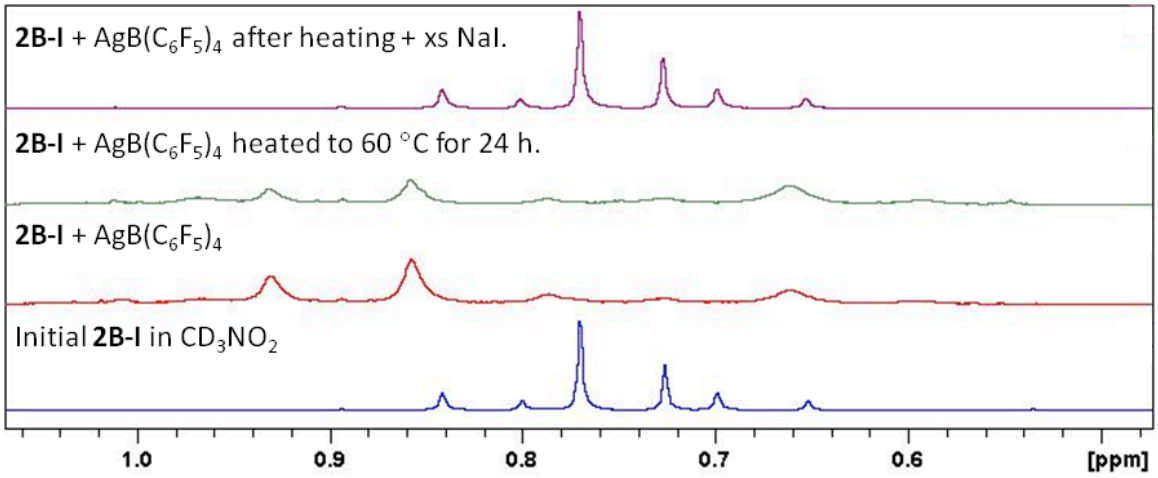


Figure S8. ^{1}H NMR spectra of the reaction between $(DAB_B)Pt^{IV}(CH_3)_3I$ (**2B-I**) and $AgB(C_6F_5)_4$ in CD_3NO_2 at 25 °C. Truncated to show the Pt–CH_3 region of the spectra.

Reactions in dichloromethane-d_2. Treating a solution of **1B** (3.9 μmol) with 1.05 equiv. of MeI in dichloromethane-d_2 produced a pale yellow-green solution after 15 min. at 25 ºC. Analysis by ^{1}H NMR at 25 °C revealed a set of peaks that are consistent with oxidative addition to make an iodide bound complex, $(DAB_B)Pt^{IV}(CH_3)_3I$, **2B-I**. ^{1}H NMR (500 MHz, 25 ºC, dichloromethane-d_2): $(DAB_B)Pt^{IV}(CH_3)_3I$ δ 0.69 (3H, s, $^2J_{195Pt-H}$ = 74.0 Hz, PtC$H_{3,ax}$), 0.83 (6H, s, $^2J_{195Pt-H}$ = 71.2 Hz, Pt(CH_3)$_{2,eq}$), 2.28 (6H, s, CCH_3), 2.37 (12H, broad s, ArCH_3), 6.40 (2H, s, Ar*H*), 6.97 (2H, s, Ar*H*),

7.25 (2H, s, Ar*H*).

Addition of $AgPF_6$ (1.05 equiv.) inside of the glove box produced a light yellow solution with a green precipitate. The ^{1}H NMR spectrum revealed a new product with a pattern consistent with $[(DAB_B)Pt^{IV}(CH_3)_3]^+$, **2B**. ^{1}H NMR (500 MHz, 25 ºC, dichloromethane-d_2): $[(DAB_B)Pt^{IV}(CH_3)_3]^+$ δ 0.93 (9H, very broad s, $^2J_{195Pt\text{-}H}$ = 79.8 Hz,), 2.37 (18H, broad s, CC*H*$_3$ and ArC*H*$_3$), 6.55 (4H, s, Ar*H*), 7.03 (2H, s, Ar*H*).

After 16 hours at 25 ºC, no ethane was observed. Solutions of **2B** were heated to 50 °C and monitored by ^{1}H NMR spectroscopy over time. After 48 hours at 50ºC, **2B** was converted to ethane, δ 0.85, and a set of new peaks possibly corresponding to $[(DAB_B)Pt^{II}(CH_3)(solv)]^+$ (**3B**), **Figure S9**. ^{1}H NMR (500 MHz, 25 ºC, dichloromethane-d_2): $[(DAB_B)Pt^{II}(CH_3)]^+$ δ 0.68 (3H, very broad s, $^2J_{195Pt\text{-}H}$ = 68.5 Hz,), Several unidentifiable broad signals centered about δ 2.35 and 6.50.

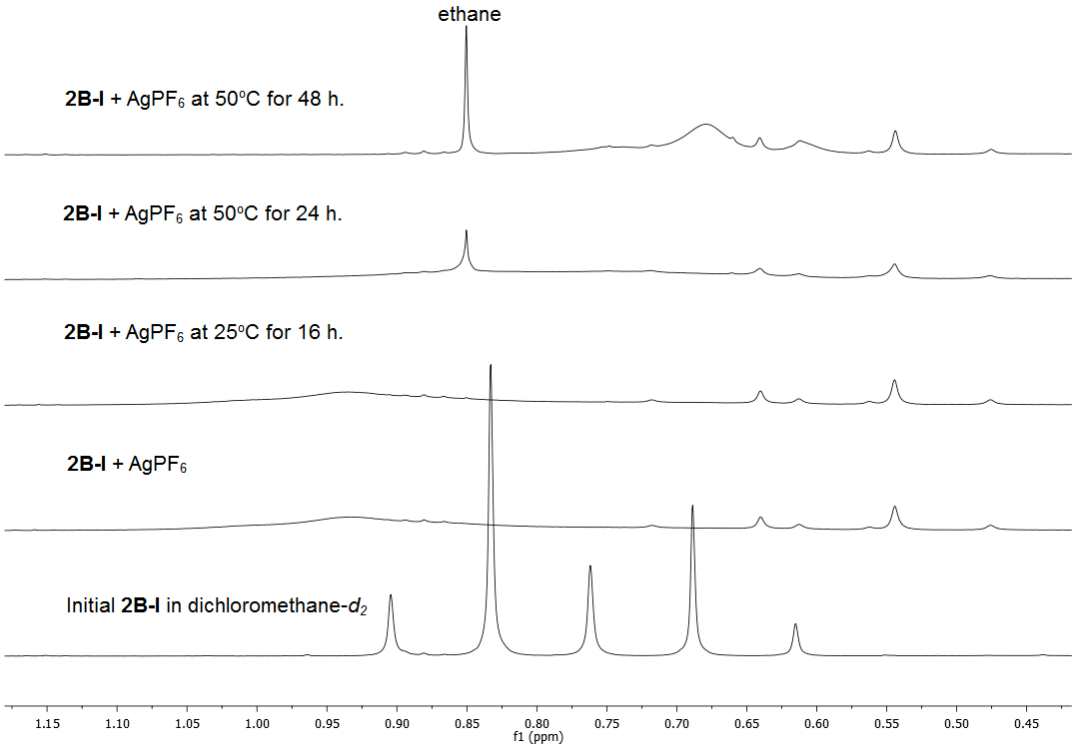


Figure S9. ^{1}H NMR spectra of the reaction between $(DAB_B)Pt^{IV}(CH_3)_3I$ (**2B-I**) and $AgPF_6$ in dichloromethane-d_2 at 50 °C. Truncated to show the Pt-CH_3 region of the spectra.

C. Reactivity of $(DAB_C)Pt^{II}(Me)_2$ (1C).

Reactions in acetone-d_6 (with CH_3I/AgX). Treating a solution of **1C** (1.8 μmol) with 1.05 equiv. of MeI in acetone-d_6 produced a pale orange-yellow solution over 5 min. at 25 ºC. By ^{1}H NMR, new peaks consistent with a tri-methyl Pt complex, $(DAB_C)Pt^{IV}(CH_3)_3I$ (**2C-I**), were observed as the major product in 89 ± 6% yield. Analysis of this complex using 2D ^{1}H/^{195}Pt NMR (gs-HMQC)[8] revealed a four bond ^{195}Pt-^{1}H coupling cross-peak and distinguished the methyl groups on the diimine carbon from those on the aryl groups, **Figure S10**. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $(DAB_C)Pt^{IV}(CH_3)_3I$ δ 1.09 (3H, s, $^2J_{195Pt\text{-}H}$ = 71.6 Hz, PtC$H_{3,ax}$), 1.13 (6H, s, $^2J_{195Pt\text{-}H}$ = 71.9 Hz, PtC$H_{3,eq}$), 2.19 (6H, s, ArCH_3), 2.47 (6H, s, CCH_3), 2.56 (6H, s, ArCH_3), 7.12 (2H, m, Ar*H*), 7.20 (4H, m, Ar*H*). ^{195}Pt NMR δ -2713.

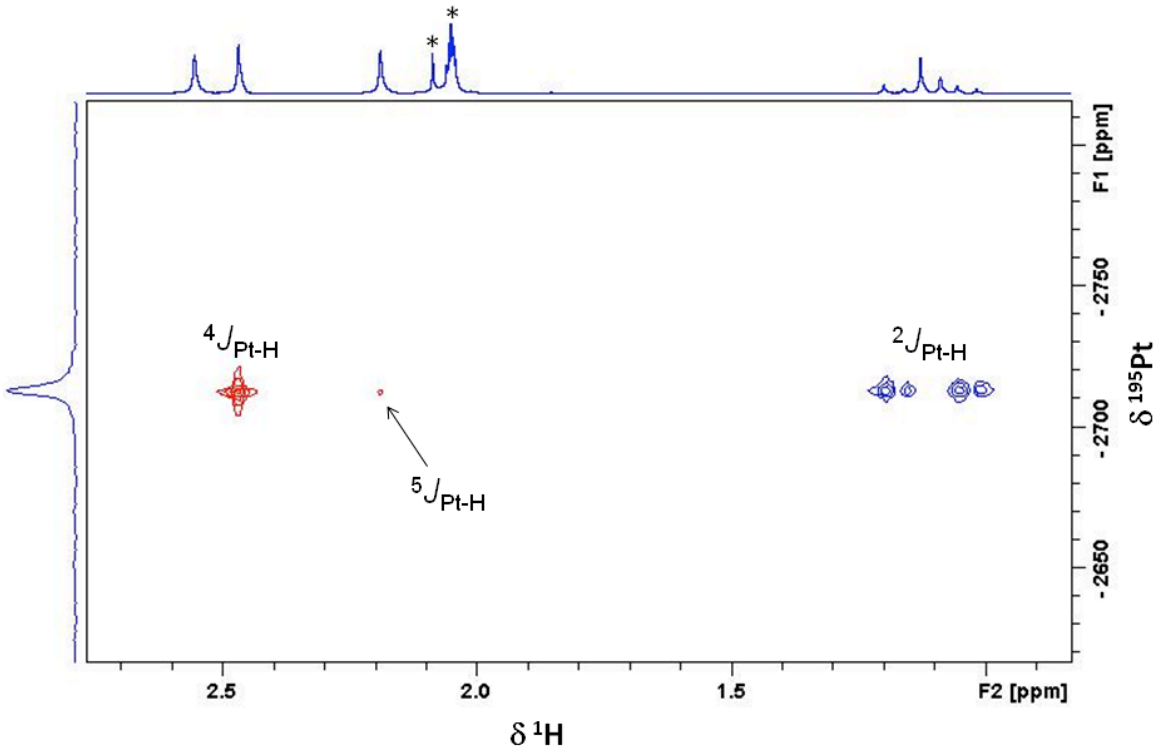


Figure S10. Overlay of ^{1}H/^{195}Pt gs-HMQC spectra of $(DAB_C)Pt^{IV}(CH_3)_3I$. Blue: the cross peaks for coupling to the three methyl groups on Pt, $^2J_{PtH}$, were found with a defocusing delay for coherence transfer (d2) of 7 ms, 3K data points and a spectral width of 5.0 kHz on F_2, and 128 time

increments and a spectral width of 64 kHz on F_1. Red: longer distance coupling, $^4J_{PtH}$ and $^5J_{PtH}$, was observed using a longer d2 of 50ms, 960 data points and spectral width of 801 Hz on F_2, and 256 time increments and a spectral width of 64 kHz on F_1.

An acetone-d_6 solution of $AgPF_6$ (1.05 equiv.) was added inside of the glove box and the solution was analyzed by ^{1}H NMR to reveal a new spectrum consistent with the cationic tri-methyl Pt^{IV} complex, $[(DAB_C)Pt^{IV}(CH_3)_3]^+$, **2C**, in 109 ± 7 % yield relative to **1C**. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ δ 0.93 (9H, s, $^2J_{195Pt-H}$ = 73.0 Hz, Pt(CH_3)$_3$), 2.18 (12H, s, ArCH_3), 2.59 (6H, s, CCH_3), 7.22 (2H, m, Ar*H*), 7.28 (4H, m, Ar*H*). ^{195}Pt NMR: δ –2725.

Solutions of **2C** were heated to 60 °C and monitored by ^{1}H NMR, **Figure S11**. Over 8.5 h., the spectrum for **2C** decreased in intensity concomitant with the formation of peaks that are consistent with ethane and the cationic mono-methyl Pt^{II} solvento complex, $[(DAB_C)Pt^{II}(CH_3)(acetone\text{-}d_6)]^+$ (**3C**), in yields of 96 ± 6 and 82 ± 6%, respectively. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $[(DAB_C)Pt^{II}(CH_3)(acetone\text{-}d_6)]^+$ δ 0.39 (3H, s, $^2J_{195Pt-H}$ = 73.4 Hz, PtCH_3), 2.08 (3H, s, CCH_3), 2.20 (3H, s, CCH_3), 2.33 (6H, s, ArCH_3), 2.39 (6H, s, ArCH_3), 7.23-7.30 (6H, m, Ar*H*). ^{195}Pt NMR: δ –2906.

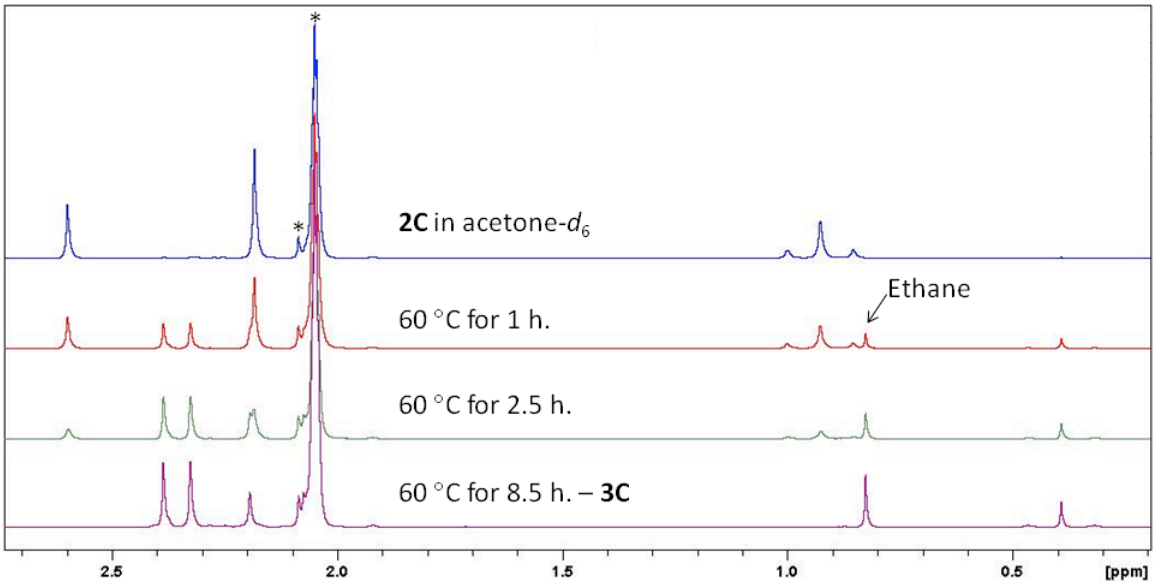


Figure S11. Selected ^{1}H NMR spectra for the conversion of $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ (**2C**) (top

spectrum) to $[(DAB_C)Pt^{II}(CH_3)(acetone\text{-}d_6)]^+$ (**3C**) and ethane (bottom spectrum) over time. Each of the spectra was acquired at 25 °C after heating for the specified time at 60 °C.

The first order rate constant for reductive-elimination was determined using solutions of **2C** (in concentrations between 1.5 and 4.5 mM in acetone-d_6), heating the solutions to 60 ºC, and collecting ^{1}H NMR spectra over time at 25 ºC. From four independent measurements, the relative integration of the methyl resonances at δ 0.93 versus internal standard were fitted to a first order equation, as shown in **Figure S12,** to provide the rate constant, k = 1.6(3) x 10^{-4} s^{-1}.

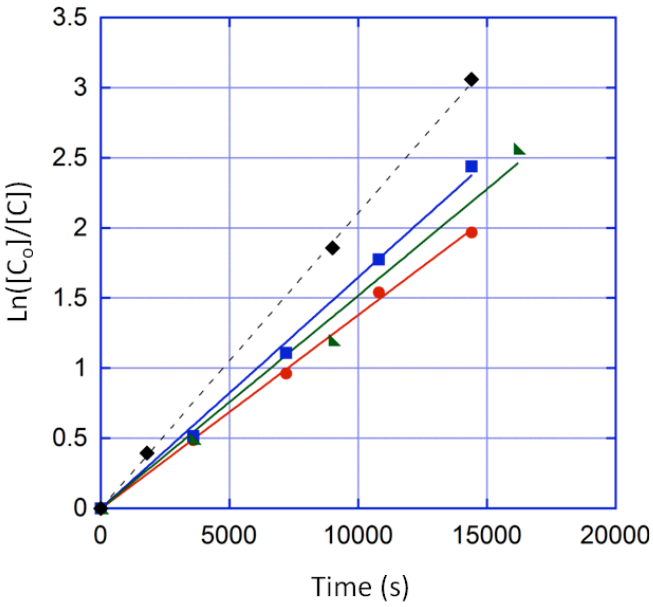


Figure S12. First order plot of $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ (**2C**) decay over time in acetone-d_6 at 60 ºC.

Evaluation of an anion affect on reductive elimination was performed by splitting one solution with **2C** (1.6 mM) into two J Young tubes and adding 20 equiv. of sodium triflate to one solution. The solutions were heated to 60 ºC and monitored, as described above, to provide the first order decay curves in **Figure S13**. With added sodium triflate, **2C** was found to decay with a first order rate constant within error of the solution having no excess triflate, k = 1.5(2) × 10^{-4} s^{-1}.

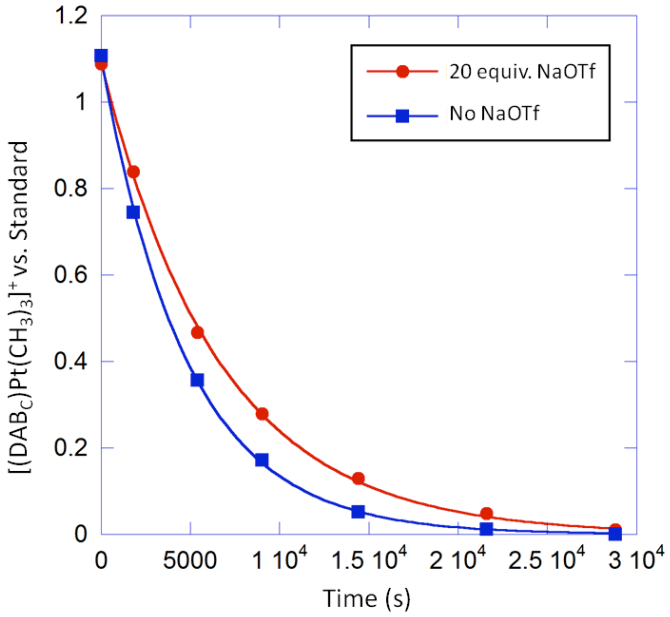
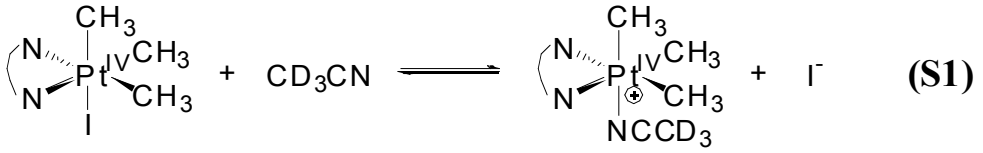


Figure S13. First order decay of $[(DAB_C)Pt^{IV}(CH_3)_3]PF_6$ (**2C**) in acetone-d_6 at 60 °C, with and without 20 equiv. sodium triflate.

Reactions in acetone-d_6 (with $AcFcPF_6$). A solution of **1C** (3.1 μmol) was treated with 1.0 equiv of $AcFcPF_6$ (3.1 μmol) in acetone-d_6 and ^{1}H NMR analysis revealed peaks matching the spectra for **2C** and **3C**, described above, in 46 ± 3 and 48 ± 3% yield, respectively. After heating to 60 °C for 8 h., **2C** was converted to ethane in 58 ± 4% yield and **3C** in an overall yield of 87 ± 6%.

Reactions in acetonitrile-d_3. In comparison to the other solvents, acetonitrile is much more strongly coordinating. Inclusion of this solvent was warranted to test the ability of the ortho methyl groups to hinder its coordination to 2C. The solubility of **1C** was very low in acetonitrile. Mixing **1C** with MeI in acetonitrile-d_3 allowed **1C** to dissolve and form a light pink solution. Analysis by ^{1}H NMR revealed a spectrum with two sets of two peaks having Pt satellites in the methyl region. The peaks within each set integrate 2:1 while the relative integration of the two sets was 11:1. In another experiment, addition of $AgPF_6$ to a similar solution precipitated AgI as a white powder; the ^{1}H NMR spectrum showed the same major set of peaks but the minor set of peaks was not present,

Figure S14. When 1.1 equiv of $AcFcPF_6$ was reacted with **1C**, complexes assigned as **2C** and **3C** were observed. The resonances assigned to **2C** match the resonances observed in the reaction **2C-I** with $AgPF_6$. Addition of 10 equiv of NaI to the **1C** + $AcFcPF_6$ reaction solution resulted in the same two sets of peaks present in the reaction of **1C** + MeI, but the ratio was now only 2.5:1. The excess iodide caused the shift in ratio of two complexes, shifting the equilibrium between iodide bound and acetonitrile bound, eq S1. The major set of peaks represent the acetonitrile bound trimethyl complex, $[(DAB_C)Pt^{IV}(CH_3)_3(CD_3CN)]I$, and was present in high enough concentration to have all the protons accounted for in the ^1H NMR spectrum. The minor set of peaks is believed to be the iodide bound trimethyl complex, $(DAB_C)Pt^{IV}(CH_3)_3I$ (**2A-I**). Due to the low solubility of the starting complex, **1C**, accurate yields were not calculated. After 20 h. at 60 °C, there was a 40% decrease in the resonances for $[(DAB_C)Pt^{IV}(CH_3)_3(CD_3CN)]PF_6$ and the simultaneous appearance of ethane, indicating that reductive elimination is significantly hindered by coordination of acetonitrile relative to the acetone solutions described above. ^1H NMR (500 MHz, 25 ºC, acetonitrile-d_3): $[(DAB_C)Pt^{IV}(CH_3)_3(CD_3CN)]^+$ δ 0.63 (6H, s, $^2J_{195Pt-H}$ = 68.7 Hz, $Pt(CH_3)_{2,eq}$), 0.83 (3H, s, $^2J_{195Pt-H}$ = 78.1 Hz, $PtCH_{3,ax}$), 2.15 (6H, s, $ArCH_3$), 2.21 (6H, s, $ArCH_3$), 2.33 (6H, s, CCH_3), 7.21 (2H, m, Ar*H*), 7.26 (4H, m, Ar*H*); $(DAB_C)Pt^{IV}(CH_3)_3I$ δ 1.06 (6H, s, $^2J_{195Pt-H}$ = 72.4 Hz, $PtCH_{3,eq}$), 1.13 (3H, s, $^2J_{195Pt-H}$ = 73.5 Hz, $PtCH_{3,ax}$). ^{195}Pt NMR (107 MHz, 25 ºC, acetonitrile-d_3): $[(DAB_C)Pt^{IV}(CH_3)_3(CD_3CN)]^+$ δ -2510; $(DAB_C)Pt^{IV}(CH_3)_3I$ δ -2708.



2-I **2** **(S1)**

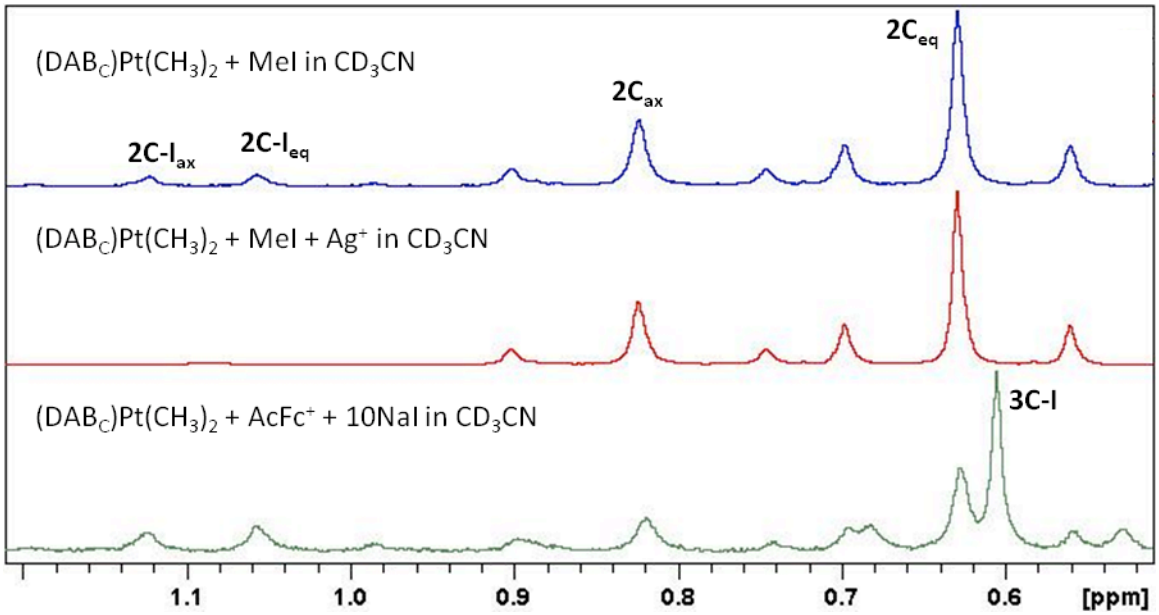


Figure S14. ^{1}H NMR spectra showing the region with resonances with ^{195}Pt satellites. In CD_3CN, **1C** was treated with: MeI (top), MeI then $AgPF_6$ (middle), and $AcFcPF_6$ then 10 equiv. of NaI (bottom). The products are identified as $(DAB_C)Pt^{IV}(CH_3)_3I$ (**2C-I**), $[(DAB_C)Pt^{IV}(CH_3)_3(CD_3CN)]^+$ (**2C**), and $(DAB_C)Pt^{II}(CH_3)I$ (**3C-I**).

Reactions in nitromethane-d_3. A 0.91 mM solution of **1C** (0.54 μmol) in nitromethane-d_3 was treated with 0.57 μmol of $AcFcPF_6$ and the solution turned to a light yellow color. Analysis by ^{1}H NMR at 25 °C revealed two sets of peaks that were analogous to those described above for **2C** and **3C** and a small amount of ethane. Monitoring the spectra every 30 min. over 13 h. revealed that **2C** converted completely to **3C** and ethane within 8 h. Fitting the disappearance of **2C** to a first order expression provided the rate constant and activation barrier to be calculated as k = 5.7(5) x 10^{-5} s^{-1} and $\Delta G^{\ddagger}$ = 23.2(1) kcal/mol. **Figure S15**. ^{1}H NMR (500 MHz, 25 ºC, nitromethane-d_3): $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ δ 0.91 (9H, s, $^2J_{195Pt-H}$ = 73.0 Hz, Pt(CH_3)$_3$), 2.11 (12H, s, ArCH_3), 2.55 (6H, s, CCH_3), 7.26 (2H, m, ArH), 7.30 (4H, m, ArH); $[(DAB_C)Pt^{II}(CH_3)(CD_3NO_2)]^+$ δ 0.51 (3H, s, $^2J_{195Pt-H}$ = 75.9 Hz, Pt(CH_3)), 2.16 (3H, s, CCH_3), 2.23 (3H, s, CCH_3), 2.32 (6H, s, ArCH_3), 2.35 (6H, s, ArCH_3), 7.12-7.17 (3H, m, ArH), 7.34 (3H, m, ArH); ethane δ 0.85.

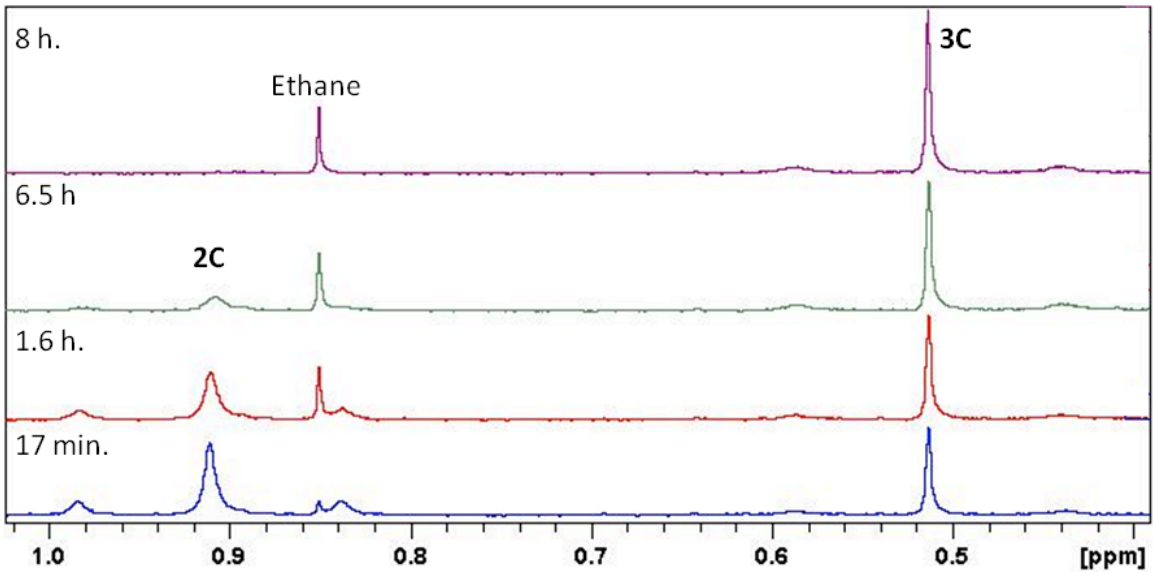


Figure S15. ^{1}H NMR spectra showing the methyl peaks with ^{195}Pt satellites and ethane. In CD_3NO_2, **1C** was treated with $AcFcPF_6$ and monitored over time. $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ (**2C**) is observed to convert to $[(DAB_C)Pt^{II}(CH_3)(CD_3NO_2)]^+$ (**3C**) and ethane.

Reactions in dichloromethane-d_2. A 3.15 mM solution of **1C** (1.89 μmol) in dichloromethane-d_2 was treated with 2.08 μmol of MeI and the solution turned to a light red color. Analysis by ^{1}H NMR at 25 °C revealed a new set of peaks analogous to those described above for **2C-I** as the major product in 75 ± 5% yield along with 19 ± 3% unreacted **1C** and MeI. ^{1}H NMR (500 MHz, 25 ºC, dichloromethane-d_2): $(DAB_C)Pt^{IV}(CH_3)_3I$ (**2C-I**) δ 1.01 (3H, s, $^{2}J_{195Pt\text{-}H}$ = 71.1 Hz, PtC$H_{3,ax}$), 1.12 (6H, s, $^{2}J_{195Pt\text{-}H}$ = 71.7 Hz, Pt(CH_3)$_{2,eq}$), 2.14 (6H, s, ArCH_3), 2.25 (6H, s, CCH_3), 2.53 (6H, s, ArCH_3), 7.12-7.22 (6H, m, ArH). 2.03 μmol of $AgPF_6$ was then added and the solution turned to a light orange color immediately and a white precipitate of AgI formed. Monitoring the spectrum over time revealed a new peak with Pt satellites (δ 1.00) that was quickly decaying to generate ethane and methane along with multiple other unidentified peaks. Methane is likely formed from decomposition of the cationic mono-methyl Pt^{II} solvento complex.[9] Estimating the half-life of this decay at 15 min. provides a rate constant and activation barrier of k = 7.6(14) x 10^{-4} s^{-1}; $\Delta G^{‡}$ =

21.7(1) kcal mol^{-1}, respectively.

D. $(DAB_D)Pt^{II}(Me)_2$ (1D).

Reactions in acetone-d_6 (with CH_3I/AgX). Treating a solution of **1D** (1.14 μmol) with 1.05 equiv. of MeI in acetone-d_6 produced a pale orange-yellow solution after 15 min. at 25 ºC. Analysis by ^{1}H NMR spectroscopy showed unreacted **1D** and MeI along with new peaks, indicating that the reaction did not proceed to completion. Addition of $AgPF_6$ (1.05 equiv.) was performed inside of the glove box and the ^{1}H NMR spectrum revealed a new product in 87 ± 6% yield, relative to **1D**, with a pattern consistent with $[(DAB_D)Pt^{II}(CH_3)_3]^+$ (**2D**) ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $[(DAB_D)Pt^{II}(CH_3)_3]^+$ δ 0.95 (9H, s, $^2J_{195Pt-H}$ = 74.1 Hz, Pt(CH_3)$_3$), 1.18 (12H, d, $^3J_{H-H}$ = 6.7 Hz, C(CH_3)$_2$), 1.30 (12H, d, $^3J_{H-H}$ = 6.7 Hz, C(CH_3)$_2$), 2.70 (4H, septet, $^3J_{H-H}$ = 6.7 Hz, CH(CH$_3$)$_2$), 2.74 (6H, s, CCH_3), 7.43-7.50 (6H, m, ArH).

Solutions of **2D** were heated to 60 °C and monitored by ^{1}H NMR spectroscopy over time. After 4.5 h., **2D** was converted to ethane and a set of new peaks corresponding to $[(DAB_D)Pt^{II}(CH_3)(acetone\text{-}d_6)]^+$ (**3D)** in yields of 91 ± 6% and 72 ± 5%, respectively. ^{1}H NMR (500 MHz, 25 ºC, acetone-d_6): $[(DAB_D)Pt^{II}(CH_3)(acetone\text{-}d_6)]^+$ δ 0.51 (3H, s, $^2J_{195Pt-H}$ = 73.4 Hz, PtCH_3), 1.21 (12H, 2 d, Δν = 2.3 Hz, $^3J_{H-H}$ = 6.7 Hz, C(CH_3)$_2$), 1.41 (12H, vt, $^3J_{H-H}$ = 7.2 Hz, C(CH_3)$_2$), 2.22 (3H, s, CCH_3), 2.32 (3H, s, CCH_3), 3.18 (2H, septet, $^3J_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 3.33 (2H, septet, $^3J_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 7.41-7.45 (6H, m, ArH).

The first order rate constant for reductive-elimination was determined using solutions of **2D** (3.0 mM in acetone-d_6), heating the solutions to 60 ºC, and collecting ^{1}H NMR spectra over time at 25 ºC. From two independent measurements, the relative integration of the methyl resonances at δ 0.95 versus internal standard were fitted to a first order equation to provide the rate constant, k =

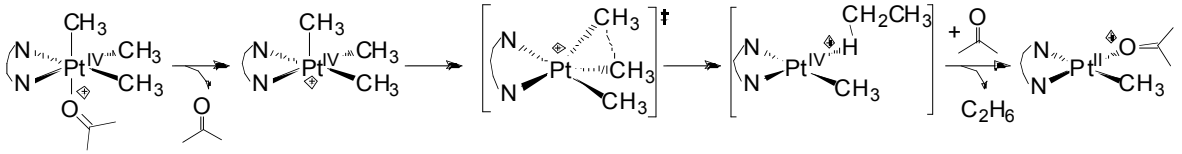
$4.2(6) \times 10^{-4}$ s^{-1}.

Reactions in acetone-d_6 (with $AcFcPF_6$). A solution of **1D** (3.1 μmol) was treated with 1.0 equiv of $AcFcPF_6$ (3.1 μmol) in acetone-d_6. Analysis of the ^1H NMR spectrum at r.t. after mixing reveals unreacted **1D** and $AcFcPF_6$ along with the initial products, **2D** and **3D**. Complete reaction of $AcFcPF_6$ provides sharp peaks for acyl ferrocene (AcFc); a broad peak downfield and in place of these sharp peaks is caused by exchange between $AcFc^+$ and AcFc. Upon mixing, only 40 ± 3% of the expected **2D** is observed along with 12 ± 1% expected **1D**, 115 ± 7% of expected **3D**, and methane, ~4%. After 8 h at 60°C, **2D** was converted to **3D** and C_2H_6, in overall yields of 68 ± 4 and 17 ± 2%, respectively.

V. Density Functional Calculations

Molecular geometries were fully optimized at the density functional level of theory (DFT) using Gaussian 03.[10] The restricted (closed shell) calculations compared three different hybrid exchange and correlation functional: B3LYP[11], B3PW91[12] and M06[13]. Atomic orbital basis functions employed a triple zeta basis set with effective core potentials and f polarization, LANL2TZ(f), [14] on Pt and for C, H, N, and O the 6-31G** basis.[15] Vibrational frequencies were calculated analytically within the harmonic oscillator approximation.[16] All minima were characterized by real frequencies unless noted otherwise.

***Scheme* S1.**



Scheme S1 illustrates the geometries of the reactants, intermediates, transition state, and products. The minimum energy geometries were optimized for acetone, ethane, the solvent bound complexes (**2B**, **2C**, **3B** and **3C**), and solvent dissociated complexes (**I-1B**, **I-1C**). Transition states were optimized as saddle points using the Berny algorithm.[17] A slight decrease in the C···C distance of the respective transitions states followed by a geometry optimization produced local minima for the C_2H_6 bound complexes, **I-2B** and **I-2C**. Calculations that included the basis set superposition error (via a counterpoise correction)[18] or polarized continuum solvation (PCM)[19] did not reveal significant errors in the calculated energies.

Representative illustrations of the calculated geometries, output Cartesian coordinates, and energy components for each calculation are presented in the following figures and tables.

Table S1. Sum of electronic and thermal **Free Energies** (Hartrees/particle).

	2B	I-1B	TS-B	I-2B	3B	Acetone	Ethane
B3LYP	-1317.5334	-1124.4191	-1124.3847	-1124.4349	-1237.7938	-193.1054	-79.7854
B3PW91	-1317.1329	-1124.0938	-1124.0632		-1237.4257	-193.0325	-79.7565
M06	-1316.5663	-1123.5740	-1123.5445		-1236.8946	-192.9698	-79.7057

	2C	I-1C	TS-C	I-2C	3C	Acetone	Ethane
B3LYP	-1317.5097	-1124.4041	-1124.3695	-1124.4206	-1237.7850	-193.1054	-79.7854
B3PW91	-1317.1088	-1124.0805	-1124.0489		-1237.4143	-193.0325	-79.7565
M06	-1316.5534	-1123.5708	-1123.5430		-1236.8964	-192.9698	-79.7057

Table S2. Sum of electronic and thermal **Enthalpies** (Hartrees/particle).

	2B	I-1B	TS-B	I-2B	3B	Acetone	Ethane
B3LYP	-1317.4239	-1124.3263	-1124.2848	-1124.3348	-1237.6929	-193.0704	-79.7578
B3PW91	-1317.0256	-1124.0027	-1123.9639		-1237.3213	-192.9972	-79.7289
M06	-1316.4530	-1123.4788	-1123.4480	-1123.4941	-1236.7923	-192.9374	-79.6782

	2C	I-1C	TS-C	I-2C	3C	Acetone	Ethane
B3LYP	-1317.4029	-1124.3121	-1124.2764	-1124.3258	-1237.6844	-193.0704	-79.7578
B3PW91	-1317.0032	-1123.9883	-1123.9561	-1124.0062	-1237.3144	-192.9972	-79.7289
M06	-1316.4501	-1123.4785	-1123.4518		-1236.7982	-192.9374	-79.6782

Table S3. ΔG_{calc} (kcal/mol) for the reaction from **2B** (top table) or **2C** (bottom table) to the listed products.

	I-1B + acetone	TS-B + acetone	I-2B to acetone	3B + ethane
B3LYP	5.59	27.15	-4.37	-28.71
B3PW91	4.13	23.33		-30.97
M06	14.11	32.68		-21.35

	I-1C + acetone	TS-C + acetone	I-2C to acetone	3C + ethane
B3LYP	0.11	21.82	-10.25	-38.09
B3PW91	-2.61	17.21		-38.88
M06	8.04	25.50		-30.56

Table S4. ΔG_{calc} (kcal/mol).

	2B --> I-1B + acetone	I-1B --> TS-B	TS-B --> I-2B	I-2B --> 3B + ethane
B3LYP	5.59	21.56	-31.51	-24.34
B3PW91	4.13	19.19		-30.97
M06	14.11	18.56		-21.35

	2C --> I-1C + acetone	I-1C --> TS-C	TS-C --> I-2C	I-2C --> 3C + ethane
B3LYP	0.11	21.72	-32.07	-27.84
B3PW91	-2.61	19.82		-38.88
M06	8.04	17.47		-30.56

Table S5. ΔH_{calc} (kcal/mol) for the reaction from **2B** (top table) or **2C** (bottom table) to the listed products.

	I-1B + acetone	TS-B + acetone	I-2B to acetone	3B + ethane
B3LYP	17.02	43.05	11.68	-16.88
B3PW91	16.13	40.52		-15.45
M06	23.03	42.41		-10.99

	I-1C + acetone	TS-C + acetone	I-2C to acetone	3C + ethane
B3LYP	12.76	35.14	4.17	-24.72
B3PW91	11.15	31.37		-25.17
M06	21.42	38.17		-16.52

Table S6. ΔH_{calc} (kcal/mol).

	2B --> I-1B + acetone	I-1B --> TS-B	TS-B --> I-2B	I-2B --> 3B + ethane
B3LYP	17.02	26.04	-31.37	-28.56
B3PW91	16.13	24.39		-15.45
M06	23.03	19.37		-10.99

	2C --> I-1C + acetone	I-1C --> TS-C	TS-C --> I-2C	I-2C --> 3C + ethane
B3LYP	12.76	22.38	-30.97	-28.89
B3PW91	11.15	20.21		-25.17
M06	21.42	16.75		-16.52

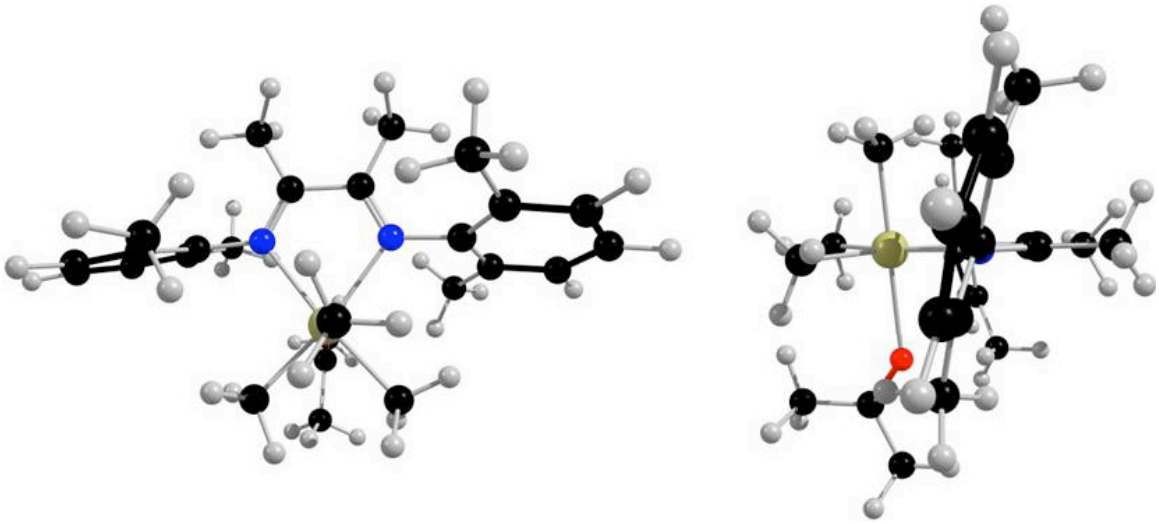


Figure S16. DFT optimized geometry of $[(DAB_C)Pt^{IV}(CH_3)_3(acetone)]^+$ (**3C**) using B3LYP and the basis sets LANL2TZ on Pt and 6-31G** on C, H, N, and O. Left: looking down the z-axis, through the $Pt\text{-}CH_{3,ax}$ bond. Right: looking along the equatorial plane, through the center of the xy-axis.

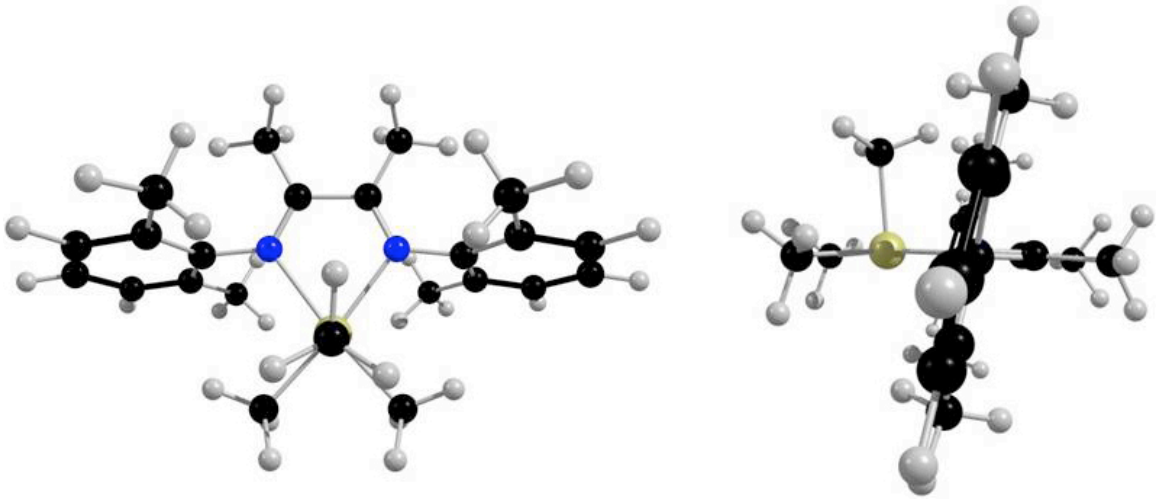


Figure S17. DFT optimized geometry of $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ (**I-1C**) using B3LYP and the basis sets LANL2TZ on Pt and 6-31G** on C, H, N, and O. Left: looking down the z-axis, through the $Pt\text{-}CH_{3,ax}$ bond. Right: looking along the equatorial plane, through the center of the xy-axis.

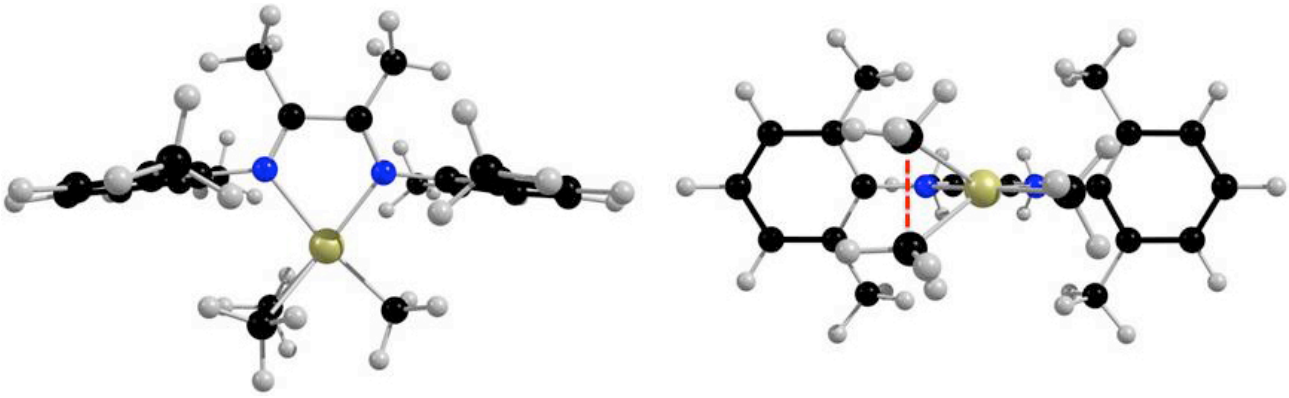


Figure S18. DFT optimized transition state (TS-C for ethane elimination from **I-1C.** Determined using B3LYP and the basis sets LANL2TZ on Pt and 6-31G** on C, H, N, and O. Left: looking down the z-axis. Right: looking along the equatorial plane, through the center of the xy-axis. The reaction coordinate frequency is highlighted with the red dashed line.

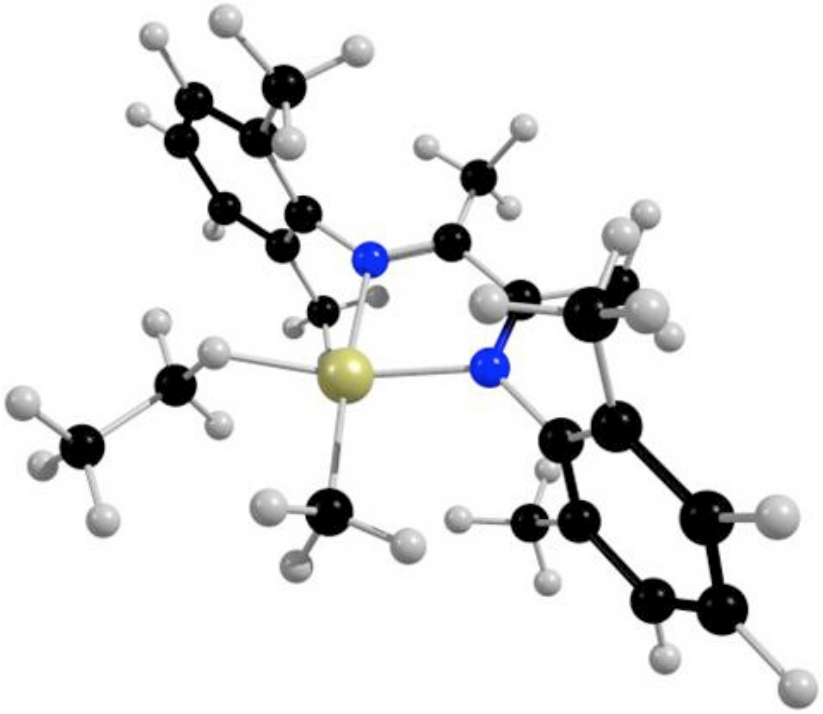


Figure S19. DFT optimized geometry for an intermediate during ethane elimination, **I-2C**. Determined using B3LYP and the basis sets LANL2TZ on Pt and 6-31G** on C, H, N, and O.

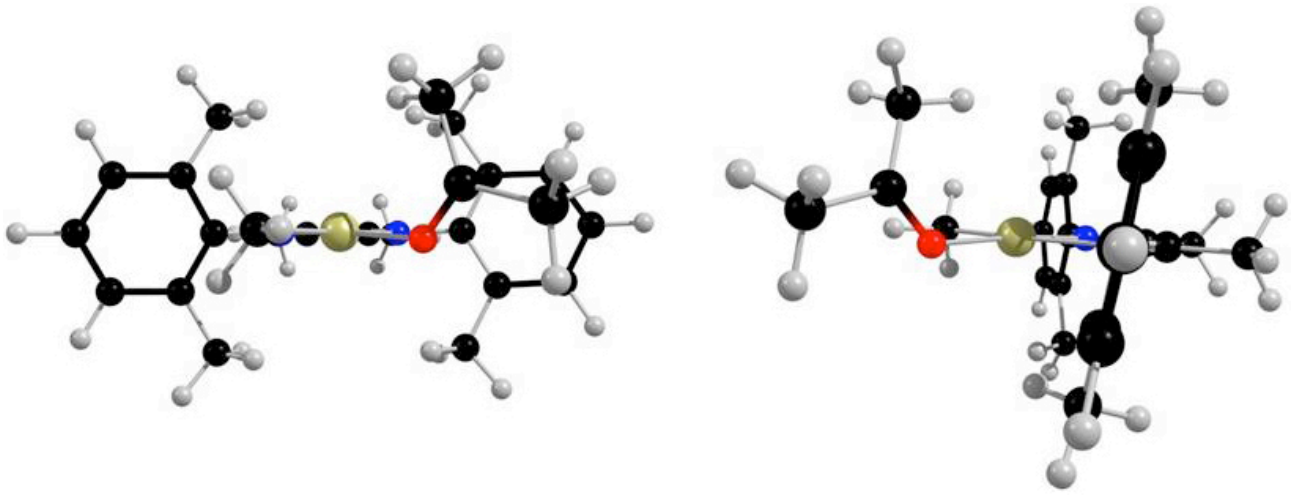


Figure S20. DFT optimized geometry for $[(DAB_C)Pt^{IV}(CH_3)(acetone)]^+$ (**4A**). Determined using B3LYP and the basis sets LANL2TZ on Pt and 6-31G** on C, H, N, and O. Left: looking along the equatorial plane, through the center of the xy-axis. Right: 90° rotation along the equatorial plane.

Table S7. DFT optimized geometries for $[(DAB_C)Pt^{IV}(CH_3)_3(acetone)]^+$ **2C** in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	y	z
6	0.8746	-1.3875	1.4480	0.8468	-1.4651	1.3970	0.8702	-1.3691	1.4843
6	-4.8281	-0.0543	1.0931	-4.8067	-0.0059	1.1157	-4.7682	0.0555	1.0540
6	3.6179	-1.6184	-0.0347	3.5836	-1.5903	-0.1215	3.6070	-1.5543	-0.0077
6	2.8773	-0.5327	0.4844	2.8446	-0.5545	0.4886	2.8450	-0.4913	0.5051
6	-0.6259	-1.5275	1.3941	-0.6487	-1.5761	1.3398	-0.6230	-1.5145	1.4318
6	-5.4743	-0.8221	0.1305	-5.4723	-0.7449	0.1458	-5.4184	-0.6829	0.0778
6	-3.3359	-1.7370	-0.5878	-3.3567	-1.6754	-0.6093	-3.3120	-1.6826	-0.5821
6	-2.6984	-0.9293	0.3784	-2.7006	-0.8934	0.3616	-2.6701	-0.9008	0.3938
6	4.8921	0.7732	0.7149	4.8492	0.7486	0.7823	4.8068	0.8806	0.6932
6	5.6378	-0.2722	0.1735	5.5905	-0.2391	0.1421	5.5772	-0.1459	0.1596
6	5.0009	-1.4515	-0.1936	4.9592	-1.3960	-0.2941	4.9777	-1.3469	-0.1836
6	3.5072	0.6716	0.8698	3.4728	0.6136	0.9672	3.4333	0.7346	0.8645
6	-4.7294	-1.6685	-0.6869	-4.7486	-1.5848	-0.6929	-4.6923	-1.5608	-0.7176
6	-3.4368	-0.1011	1.2517	-3.4171	-0.0743	1.2575	-3.3885	-0.0479	1.2482
7	1.4403	-0.6167	0.5760	1.4135	-0.6437	0.5751	1.4227	-0.6104	0.6007
7	-1.2537	-0.9173	0.4422	-1.2619	-0.9032	0.4217	-1.2396	-0.9307	0.4633
78	0.0333	0.3304	-0.9129	0.0386	0.3396	-0.8657	0.0355	0.2831	-0.9198
6	-1.4518	0.9643	-2.1815	-1.4226	0.9925	-2.1291	-1.4302	0.8886	-2.2103

6	1.3684	1.4740	-1.9767	1.4275	1.4443	-1.8737	1.3621	1.3961	-2.0091
1	-5.4061	0.5883	1.7514	-5.3692	0.6306	1.7937	-5.3351	0.7226	1.7016
1	-6.5537	-0.7746	0.0276	-6.5523	-0.6808	0.0550	-6.4932	-0.5899	-0.0524
1	5.3877	1.6883	1.0259	5.3421	1.6432	1.1534	5.2741	1.8193	0.9849
1	6.7110	-0.1693	0.0480	6.6585	-0.1117	-0.0054	6.6462	-0.0098	0.0198
1	5.5794	-2.2740	-0.6048	5.5372	-2.1795	-0.7770	5.5766	-2.1593	-0.5920
1	-5.2313	-2.2955	-1.4181	-5.2664	-2.1917	-1.4306	-5.2004	-2.1722	-1.4609
1	-1.0750	1.5958	-2.9900	-1.0320	1.4909	-3.0206	-1.0574	1.5396	-3.0091
1	-2.1856	1.5181	-1.5877	-2.0769	1.6779	-1.5806	-2.1864	1.4164	-1.6129
1	-1.9551	0.1006	-2.6224	-2.0289	0.1404	-2.4473	-1.9070	0.0147	-2.6684
1	1.2403	1.3624	-3.0554	1.1511	1.6368	-2.9136	1.2580	1.2298	-3.0861
1	2.3819	1.1676	-1.7031	2.3835	0.9133	-1.8559	2.3772	1.1148	-1.6982
1	1.2286	2.5262	-1.7149	1.5580	2.3984	-1.3536	1.2000	2.4602	-1.8002
6	1.6171	-2.1387	2.5196	1.5866	-2.2928	2.4023	1.6162	-2.0912	2.5557
1	1.5982	-3.2171	2.3252	1.5403	-3.3562	2.1409	1.6116	-3.1737	2.3714
1	2.6567	-1.8192	2.5727	2.6349	-1.9995	2.4541	2.6551	-1.7585	2.6049
1	1.1460	-1.9810	3.4938	1.1371	-2.1872	3.3940	1.1449	-1.9337	3.5316
6	-1.2957	-2.3858	2.4326	-1.3338	-2.4666	2.3302	-1.2989	-2.3263	2.4852
1	-1.2232	-1.9241	3.4238	-1.2222	-2.0739	3.3470	-1.2547	-1.8196	3.4582
1	-2.3486	-2.5348	2.1983	-2.3968	-2.5557	2.1082	-2.3487	-2.4961	2.2353
1	-0.8048	-3.3611	2.4990	-0.8841	-3.4644	2.3244	-0.8011	-3.2941	2.6092
6	3.0159	-2.9586	-0.3954	2.9926	-2.9047	-0.5640	3.0371	-2.9009	-0.3492
1	1.9432	-2.9153	-0.5826	3.3506	-3.1727	-1.5622	3.4556	-3.2678	-1.2925
1	3.4917	-3.3604	-1.2941	3.3075	-3.7094	0.1112	3.3006	-3.6407	0.4185
1	3.1876	-3.6891	0.4050	1.9034	-2.9023	-0.5964	1.9484	-2.9003	-0.4536
6	2.7351	1.8246	1.4620	2.7193	1.6562	1.7457	2.6201	1.8553	1.4362
1	3.4146	2.5170	1.9647	3.1965	2.6346	1.6447	3.2710	2.6120	1.8840
1	2.2039	2.3814	0.6844	1.6781	1.7385	1.4324	2.0210	2.3442	0.6565
1	1.9855	1.4964	2.1875	2.7167	1.4092	2.8152	1.9164	1.5117	2.2047
6	-2.5761	-2.6942	-1.4742	-2.6228	-2.6256	-1.5164	-2.5560	-2.6636	-1.4247
1	-3.2626	-3.4060	-1.9380	-3.3203	-3.3396	-1.9603	-3.2448	-3.3332	-1.9472
1	-2.0493	-2.1742	-2.2792	-2.1241	-2.1026	-2.3381	-1.9405	-2.1662	-2.1839
1	-1.8288	-3.2697	-0.9182	-1.8569	-3.1993	-0.9851	-1.8800	-3.2857	-0.8230
6	-2.8037	0.6887	2.3745	-2.7552	0.6767	2.3828	-2.7594	0.7041	2.3853
1	-1.7866	1.0085	2.1471	-1.7580	1.0338	2.1214	-1.6917	0.8923	2.2413
1	-3.4006	1.5781	2.5953	-3.3627	1.5380	2.6733	-3.2558	1.6711	2.5257
1	-2.7742	0.0982	3.2992	-2.6652	0.0452	3.2759	-2.8861	0.1548	3.3285
6	0.5179	-1.1627	-2.2266	0.4759	-1.1345	-2.1966	0.5535	-1.2228	-2.1888
1	0.1974	-2.1213	-1.8161	0.1401	-2.0950	-1.8003	0.2297	-2.1736	-1.7505
1	0.0311	-0.9953	-3.1885	-0.0195	-0.9404	-3.1501	0.0833	-1.0849	-3.1674
1	1.6004	-1.1615	-2.3668	1.5556	-1.1598	-2.3560	1.6425	-1.2193	-2.3079
6	-0.6657	3.2993	0.5944	-0.6035	3.3095	0.5087	-0.6862	3.1902	0.5716
8	-0.4066	2.0920	0.5918	-0.3952	2.0942	0.5807	-0.4705	1.9793	0.5836

6	-0.8071	4.0200	1.9111	-0.8289	4.0866	1.7741	-0.8327	3.9242	1.8652
6	-0.8510	4.1190	-0.6533	-0.6468	4.0768	-0.7768	-0.7769	4.0018	-0.6779
1	-0.4559	3.3996	2.7356	-0.6323	3.4727	2.6529	-0.5929	3.2788	2.7129
1	-0.9199	3.5016	-1.5455	-0.5477	3.4319	-1.6461	-0.9535	3.3829	-1.5591
1	-1.8640	4.2673	2.0709	-1.8682	4.4359	1.8011	-1.8623	4.2912	1.9638
1	-0.2632	4.9699	1.8932	-0.2003	4.9828	1.7924	-0.1889	4.8120	1.8716
1	-0.0008	4.8057	-0.7520	0.1605	4.8188	-0.7756	0.1744	4.5373	-0.8070
1	-1.7432	4.7471	-0.5602	-1.5821	4.6446	-0.8356	-1.5526	4.7694	-0.5888

Table S8. DFT optimized geometries for $[(DAB_C)Pt^{IV}(CH_3)_3]^+$ (**I-1C**) in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	y	z
6	-0.7571	1.8115	0.3820	-0.7537	1.7941	0.4066	-0.7502	1.8772	0.2582
6	4.7287	-0.2020	1.3870	4.6932	-0.2586	1.3951	4.5850	-0.3704	1.4523
6	-3.5681	0.9163	-0.9213	-3.5603	0.9265	-0.8892	-3.5762	0.7397	-0.9281
6	-2.7825	0.5581	0.1917	-2.7640	0.5370	0.2026	-2.7399	0.5714	0.1806
6	0.7550	1.8120	0.3852	0.7512	1.7946	0.4105	0.7526	1.8754	0.2757
6	5.5281	0.1611	0.3056	5.5032	0.1355	0.3352	5.4334	-0.0334	0.4024
6	3.5661	0.9401	-0.9092	3.5579	0.9508	-0.8763	3.5697	0.9128	-0.8326
6	2.7814	0.5589	0.1970	2.7629	0.5381	0.2083	2.7362	0.5497	0.2341
6	-4.7285	-0.1758	1.4003	-4.6924	-0.2318	1.4100	-4.5729	-0.1279	1.5496
6	-5.5295	0.1678	0.3138	-5.5044	0.1428	0.3447	-5.4325	0.0479	0.4718
6	-4.9503	0.7088	-0.8313	-4.9392	0.7162	-0.7892	-4.9356	0.4765	-0.7522
6	-3.3422	0.0074	1.3617	-3.3088	-0.0471	1.3607	-3.2088	0.1268	1.4243
6	4.9478	0.7261	-0.8272	4.9364	0.7333	-0.7851	4.9269	0.5982	-0.7234
6	3.3427	-0.0168	1.3545	3.3098	-0.0716	1.3525	3.2228	-0.0980	1.3834
7	-1.3451	0.6867	0.1389	-1.3344	0.6705	0.1430	-1.3246	0.7433	0.0524
7	1.3444	0.6868	0.1477	1.3335	0.6705	0.1531	1.3225	0.7262	0.1614
78	-0.0010	-1.0562	-0.2349	-0.0011	-1.0270	-0.2606	-0.0232	-1.0131	-0.2296
6	1.3995	-2.5399	-0.3848	1.3863	-2.4993	-0.4530	1.3162	-2.5510	-0.3376
6	-1.4068	-2.5321	-0.3968	-1.3952	-2.4894	-0.4694	-1.4569	-2.4236	-0.5322
1	5.1794	-0.6379	2.2738	5.1338	-0.7212	2.2736	4.9808	-0.8580	2.3410
1	6.6012	0.0039	0.3453	6.5758	-0.0239	0.3818	6.4930	-0.2656	0.4643
1	-5.1780	-0.5934	2.2964	-5.1316	-0.6757	2.2989	-4.9590	-0.4711	2.5075
1	-6.6029	0.0148	0.3593	-6.5774	-0.0117	0.3979	-6.4938	-0.1553	0.5851
1	-5.5748	0.9781	-1.6780	-5.5736	1.0090	-1.6211	-5.6074	0.6064	-1.5984
1	5.5709	1.0100	-1.6701	5.5691	1.0408	-1.6129	5.5900	0.8612	-1.5457
1	1.1836	-3.2627	-1.1742	1.1783	-3.1938	-1.2705	1.1966	-3.1603	-1.2390
1	1.4041	-3.0715	0.5759	1.3801	-3.0713	0.4850	1.1529	-3.1945	0.5383
1	2.3830	-2.0930	-0.5531	2.3763	-2.0549	-0.5931	2.3323	-2.1357	-0.3083
1	-1.1724	-3.2743	-1.1625	-1.1581	-3.2144	-1.2517	-1.1444	-3.2400	-1.1900

1	-2.3826	-2.0842	-0.6032	-2.3738	-2.0421	-0.6679	-2.3569	-1.9396	-0.9329
1	-1.4429	-3.0411	0.5758	-1.4373	-3.0277	0.4878	-1.6883	-2.8404	0.4604
6	-1.4725	3.0917	0.7092	-1.4729	3.0569	0.7617	-1.4762	3.1460	0.5464
1	-1.1975	3.8795	-0.0001	-1.2010	3.8642	0.0735	-1.1358	3.9511	-0.1150
1	-2.5526	2.9584	0.6871	-2.5530	2.9175	0.7348	-2.5545	3.0197	0.4305
1	-1.1838	3.4475	1.7041	-1.1886	3.3899	1.7658	-1.2781	3.4763	1.5744
6	1.4681	3.0932	0.7135	1.4675	3.0584	0.7674	1.4760	3.1600	0.4880
1	1.1458	3.4720	1.6891	1.1480	3.4151	1.7523	1.0493	3.7192	1.3272
1	2.5471	2.9511	0.7329	2.5466	2.9093	0.7839	2.5370	2.9861	0.6807
1	1.2264	3.8682	-0.0219	1.2300	3.8533	0.0523	1.3861	3.8016	-0.3987
6	-2.9704	1.5039	-2.1784	-2.9761	1.5438	-2.1318	-3.0333	1.1532	-2.2625
1	-2.2588	0.8195	-2.6498	-2.2828	0.8635	-2.6352	-2.4174	0.3576	-2.7039
1	-3.7540	1.7162	-2.9085	-3.7671	1.7905	-2.8430	-3.8440	1.3641	-2.9652
1	-2.4416	2.4451	-1.9895	-2.4306	2.4708	-1.9222	-2.4059	2.0521	-2.2048
6	-2.4875	-0.3507	2.5539	-2.4394	-0.4371	2.5251	-2.2641	-0.0780	2.5706
1	-3.0886	-0.8293	3.3298	-3.0276	-0.9366	3.2977	-2.7874	-0.4716	3.4463
1	-1.6828	-1.0476	2.2879	-1.6414	-1.1285	2.2255	-1.4647	-0.7962	2.3208
1	-2.0143	0.5311	3.0022	-1.9573	0.4312	2.9891	-1.7652	0.8521	2.8755
6	2.9695	1.5668	-2.1481	2.9751	1.6090	-2.0986	3.0701	1.6258	-2.0549
1	3.7314	1.6779	-2.9222	3.7426	1.7367	-2.8647	3.6181	1.2985	-2.9440
1	2.1593	0.9630	-2.5657	2.1661	1.0186	-2.5367	2.0040	1.4592	-2.2421
1	2.5639	2.5665	-1.9516	2.5728	2.6053	-1.8800	3.2251	2.7102	-1.9736
6	2.4902	-0.3955	2.5419	2.4427	-0.4829	2.5112	2.2975	-0.4587	2.5056
1	1.6842	-1.0866	2.2654	1.6472	-1.1725	2.2013	1.5397	-1.1927	2.1871
1	3.0926	-0.8886	3.3077	3.0334	-0.9924	3.2755	2.8462	-0.9030	3.3406
1	2.0193	0.4790	3.0066	1.9581	0.3766	2.9886	1.7523	0.4138	2.8898
6	0.0241	-0.8540	-2.2771	0.0273	-0.7736	-2.2795	0.2502	-0.7809	-2.2390
1	-0.0380	0.2155	-2.4778	-0.0413	0.3008	-2.4560	-0.1103	0.2265	-2.4738
1	0.9566	-1.2766	-2.6502	0.9630	-1.1805	-2.6644	1.3210	-0.8857	-2.4362
1	-0.8350	-1.3855	-2.6856	-0.8271	-1.2995	-2.7068	-0.3260	-1.5441	-2.7676

Table S9. DFT optimized geometries for **TS-C** in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	y	z
6	0.7101	1.8902	0.0189	0.7039	1.8833	0.0095	0.7052	1.9080	0.2297
6	-4.8278	0.2753	-1.2047	-4.8046	0.2503	-1.2089	-4.7383	0.3240	-1.2747
6	3.4079	0.5230	1.2375	3.3856	0.5162	1.2321	3.4172	0.3548	1.2216
6	2.7360	0.6195	0.0030	2.7141	0.6044	-0.0008	2.7076	0.6273	0.0446
6	-0.7830	1.8440	0.0168	-0.7827	1.8386	0.0073	-0.7849	1.8637	0.2222
6	-5.5165	0.1671	0.0015	-5.4947	0.1546	-0.0046	-5.4583	0.0642	-0.1149
6	-3.4349	0.4072	1.2375	-3.4190	0.4053	1.2322	-3.4436	0.2734	1.2152

6	-2.7702	0.5179	0.0031	-2.7538	0.5057	-0.0002	-2.7504	0.5346	0.0286
6	4.7942	0.3329	-1.2045	4.7668	0.3082	-1.2077	4.6880	0.4164	-1.2797
6	5.4825	0.2188	0.0015	5.4552	0.2022	-0.0031	5.4158	0.1274	-0.1317
6	4.7929	0.3182	1.2079	4.7684	0.3103	1.2019	4.7847	0.1038	1.1057
6	3.4091	0.5366	-1.2325	3.3839	0.5130	-1.2351	3.3186	0.6742	-1.2171
6	-4.8235	0.2324	1.2082	-4.8055	0.2301	1.2015	-4.8152	0.0408	1.1164
6	-3.4394	0.4515	-1.2324	-3.4182	0.4262	-1.2350	-3.3652	0.5628	-1.2285
7	1.2998	0.7382	-0.0001	1.2853	0.7276	-0.0044	1.2865	0.7646	0.1099
7	-1.3267	0.6604	0.0027	-1.3186	0.6524	0.0005	-1.3226	0.6925	0.0862
78	-0.0634	-0.9625	-0.0140	-0.0573	-0.9477	-0.0067	-0.0573	-0.9403	-0.0510
6	-1.5660	-2.3702	-0.0195	-1.5447	-2.3518	0.0028	-1.5379	-2.3545	-0.1959
6	1.3041	-2.4310	-0.9768	1.2773	-2.3972	-0.9592	1.3219	-2.2773	-1.1068
1	-5.3681	0.2213	-2.1453	-5.3428	0.1856	-2.1504	-5.2417	0.3384	-2.2394
1	-6.5930	0.0290	0.0009	-6.5715	0.0159	-0.0062	-6.5270	-0.1242	-0.1715
1	5.3332	0.2683	-2.1452	5.3048	0.2364	-2.1490	5.1837	0.4462	-2.2482
1	6.5557	0.0572	0.0011	6.5285	0.0393	-0.0036	6.4810	-0.0757	-0.2015
1	5.3311	0.2419	2.1483	5.3080	0.2397	2.1424	5.3568	-0.1086	2.0069
1	-5.3606	0.1452	2.1481	-5.3447	0.1500	2.1414	-5.3791	-0.1648	2.0241
1	-1.1915	-3.3817	-0.2035	-1.1705	-3.3657	-0.1727	-1.1833	-3.2765	-0.6721
1	-2.2947	-2.1213	-0.7954	-2.2779	-2.1139	-0.7735	-2.3747	-1.9514	-0.7783
1	-2.0740	-2.3567	0.9502	-2.0532	-2.3327	0.9728	-1.8963	-2.5959	0.8135
1	1.2999	-3.5172	-0.9770	1.2525	-3.4841	-0.9593	1.3345	-3.3614	-1.2093
1	2.3005	-2.0241	-1.1182	2.2811	-2.0108	-1.1138	2.3246	-1.8512	-1.1698
1	0.6432	-2.1247	-1.8038	0.6194	-2.0867	-1.7921	0.6994	-1.9083	-1.9443
6	1.4134	3.2159	0.0437	1.4139	3.1981	0.0279	1.4100	3.2136	0.3543
1	1.1308	3.7866	0.9349	1.1382	3.7743	0.9178	1.1245	3.7226	1.2829
1	2.4949	3.0864	0.0399	2.4949	3.0592	0.0220	2.4938	3.0768	0.3494
1	1.1284	3.8206	-0.8241	1.1319	3.8022	-0.8412	1.1384	3.8844	-0.4701
6	-1.5583	3.1274	0.0338	-1.5625	3.1115	0.0152	-1.5573	3.1280	0.3533
1	-1.3003	3.7395	-0.8375	-1.3093	3.7197	-0.8603	-1.2944	3.8251	-0.4519
1	-2.6315	2.9484	0.0319	-2.6351	2.9235	0.0144	-2.6333	2.9477	0.3237
1	-1.2999	3.7161	0.9209	-1.3090	3.7087	0.8981	-1.3098	3.6304	1.2967
6	2.6857	0.6826	2.5550	2.6659	0.6885	2.5435	2.7414	0.3778	2.5595
1	1.7419	0.1303	2.5847	1.6916	0.1911	2.5549	1.7725	-0.1376	2.5464
1	3.3092	0.3334	3.3809	3.2614	0.2887	3.3673	3.3670	-0.0924	3.3234
1	2.4466	1.7348	2.7550	2.4875	1.7489	2.7616	2.5461	1.4066	2.8923
6	2.6831	0.7052	-2.5471	2.6563	0.6782	-2.5431	2.5322	1.0120	-2.4486
1	3.3304	0.4277	-3.3818	3.2662	0.3156	-3.3735	3.1174	0.8167	-3.3514
1	1.7763	0.0949	-2.6036	1.7031	0.1407	-2.5598	1.5986	0.4372	-2.5175
1	2.3785	1.7468	-2.7073	2.4338	1.7334	-2.7442	2.2518	2.0741	-2.4697
6	-2.6941	0.4816	2.5510	-2.6785	0.4905	2.5390	-2.7357	0.2455	2.5351
1	-3.3703	0.2801	3.3843	-3.3445	0.2637	3.3741	-3.4143	-0.0605	3.3359
1	-1.8756	-0.2455	2.5963	-1.8395	-0.2136	2.5743	-1.8869	-0.4530	2.5251

1	-2.2550	1.4723	2.7202	-2.2676	1.4922	2.7134	-2.3332	1.2308	2.8068
6	-2.7021	0.5697	-2.5447	-2.6748	0.5292	-2.5389	-2.5720	0.8218	-2.4730
1	-1.8887	-0.1609	-2.6190	-1.8426	-0.1827	-2.5852	-1.7397	0.1100	-2.5756
1	-3.3820	0.4032	-3.3827	-3.3412	0.3244	-3.3792	-3.2016	0.7329	-3.3623
1	-2.2564	1.5627	-2.6790	-2.2530	1.5296	-2.6939	-2.1325	1.8284	-2.4832
6	1.2166	-2.5062	0.9755	1.2082	-2.4492	0.9773	1.1649	-2.5513	0.8161
1	0.8678	-1.8764	1.8094	0.8428	-1.8278	1.8158	0.7986	-2.0285	1.7208
1	0.7823	-3.4941	1.0857	0.7985	-3.4471	1.1005	0.7329	-3.5505	0.8088
1	2.3021	-2.5200	1.0113	2.2944	-2.4349	1.0188	2.2527	-2.5710	0.8802

Table S10. DFT optimized geometries for $[(DAB_C)Pt^{IV}(CH_3)(acetone)]^+$ (**3C**) in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	Y	z
6	1.1651	-1.9401	0.1784	1.1554	-1.9360	0.1801	-1.2264	1.9294	-0.0684
6	-4.5506	-1.1030	1.1733	-4.5363	-1.0867	1.1643	4.3536	1.0383	1.2712
6	3.6382	-0.3301	-1.1737	3.6134	-0.3249	-1.1737	-3.6987	0.0848	-1.1015
6	2.9508	-0.3511	0.0528	2.9283	-0.3480	0.0515	-2.9621	0.2980	0.0678
6	-0.3026	-2.1849	0.1510	-0.3064	-2.1751	0.1528	0.2327	2.1904	-0.1192
6	-5.2346	-1.0363	-0.0385	-5.2164	-1.0166	-0.0473	5.1155	0.7947	0.1338
6	-3.1266	-1.0641	-1.2535	-3.1093	-1.0397	-1.2563	3.1223	0.8655	-1.2445
6	-2.4616	-1.1484	-0.0144	-2.4488	-1.1277	-0.0175	2.3802	1.1173	-0.0820
6	4.9072	0.3565	1.2438	4.8819	0.3521	1.2426	-4.7968	-0.3572	1.4445
6	5.6186	0.3827	0.0461	5.5922	0.3791	0.0465	-5.5587	-0.5774	0.3032
6	4.9871	0.0430	-1.1486	4.9610	0.0447	-1.1478	-5.0131	-0.3575	-0.9554
6	3.5564	-0.0088	1.2744	3.5325	-0.0105	1.2724	-3.4771	0.0829	1.3511
6	-4.5249	-1.0186	-1.2382	-4.5055	-0.9944	-1.2440	4.5023	0.7160	-1.1122
6	-3.1520	-1.1628	1.2137	-3.1397	-1.1465	1.2075	2.9706	1.2112	1.1880
7	1.5401	-0.6948	0.0503	1.5252	-0.6906	0.0485	-1.5776	0.6756	-0.0470
7	-1.0241	-1.1202	-0.0080	-1.0180	-1.1046	-0.0093	0.9589	1.1256	-0.1721
78	0.1194	0.6887	-0.1897	0.1165	0.6770	-0.1908	-0.1450	-0.7108	-0.2004
6	1.3740	2.3076	-0.3222	1.3675	2.2814	-0.3256	-1.3410	-2.3687	-0.1567
1	-5.1031	-1.1134	2.1087	-5.0911	-1.1002	2.0988	4.8334	1.1066	2.2462
1	-6.3194	-0.9972	-0.0483	-6.3015	-0.9778	-0.0592	6.1924	0.6730	0.2180
1	5.3994	0.6254	2.1738	5.3747	0.6191	2.1735	-5.2235	-0.5339	2.4299
1	6.6648	0.6719	0.0432	6.6391	0.6668	0.0441	-6.5839	-0.9257	0.3957
1	5.5411	0.0688	-2.0823	5.5150	0.0729	-2.0819	-5.6097	-0.5334	-1.8484
1	-5.0580	-0.9677	-2.1832	-5.0367	-0.9403	-2.1904	5.0984	0.5355	-2.0049
1	0.8181	3.2300	-0.5232	0.8183	3.2091	-0.5237	-0.7648	-3.2535	0.1441

1	2.0894	2.1607	-1.1378	2.0795	2.1343	-1.1451	-1.7362	-2.5467	-1.1666
1	1.9434	2.4346	0.6054	1.9458	2.4072	0.5973	-2.1877	-2.2399	0.5281
6	2.1107	-3.0911	0.3461	2.1015	-3.0780	0.3499	-2.1837	3.0658	-0.0089
1	2.0264	-3.7785	-0.5038	2.0120	-3.7748	-0.4916	-2.0736	3.7036	-0.8949
1	3.1437	-2.7565	0.4196	3.1345	-2.7381	0.4101	-3.2178	2.7209	0.0468
1	1.8582	-3.6657	1.2435	1.8600	-3.6442	1.2558	-1.9771	3.6992	0.8629
6	-0.8371	-3.5793	0.2971	-0.8508	-3.5588	0.2984	0.7571	3.5828	-0.0852
1	-0.5882	-3.9896	1.2824	-0.5976	-3.9756	1.2796	0.4846	4.0863	0.8511
1	-1.9198	-3.5982	0.1759	-1.9352	-3.5665	0.1853	1.8458	3.5917	-0.1816
1	-0.3865	-4.2441	-0.4470	-0.4130	-4.2253	-0.4522	0.3276	4.1777	-0.8999
6	2.9598	-0.6920	-2.4730	2.9307	-0.6816	-2.4660	-3.0941	0.3203	-2.4514
1	2.0509	-0.1009	-2.6312	2.0048	-0.1112	-2.6018	-2.1540	-0.2350	-2.5745
1	3.6296	-0.5160	-3.3171	3.5841	-0.4755	-3.3162	-3.7784	0.0086	-3.2451
1	2.6671	-1.7485	-2.5039	2.6649	-1.7446	-2.5092	-2.8620	1.3810	-2.6176
6	2.7900	-0.0396	2.5745	2.7640	-0.0464	2.5649	-2.6307	0.2910	2.5696
1	3.3898	0.3810	3.3844	3.3415	0.4123	3.3705	-3.1922	0.0603	3.4790
1	1.8587	0.5332	2.5042	1.8108	0.4872	2.4782	-1.7388	-0.3527	2.5479
1	2.5184	-1.0616	2.8658	2.5327	-1.0733	2.8732	-2.2726	1.3258	2.6571
6	-2.3636	-1.0428	-2.5556	-2.3414	-1.0189	-2.5493	2.4426	0.7787	-2.5753
1	-3.0449	-0.9159	-3.3996	-3.0113	-0.8480	-3.3948	3.1575	0.5450	-3.3689
1	-1.6341	-0.2253	-2.5796	-1.5805	-0.2300	-2.5509	1.6624	0.0047	-2.5773
1	-1.8081	-1.9740	-2.7179	-1.8217	-1.9676	-2.7277	1.9513	1.7247	-2.8387
6	-2.4265	-1.2417	2.5370	-2.4168	-1.2332	2.5258	2.1489	1.4738	2.4159
1	-1.5724	-0.5574	2.5794	-1.5275	-0.5946	2.5509	1.2351	0.8633	2.4419
1	-3.1013	-0.9946	3.3598	-3.0741	-0.9343	3.3457	2.7248	1.2616	3.3220
1	-2.0410	-2.2498	2.7327	-2.0858	-2.2565	2.7409	1.8348	2.5243	2.4791
6	-2.0567	2.7694	0.1711	-2.0227	2.7551	0.1830	2.2952	-2.3911	0.2870
8	-1.4510	1.9685	-0.5634	-1.4325	1.9548	-0.5624	1.4711	-1.9570	-0.5316
6	-3.1929	3.5457	-0.4187	-3.1467	3.5503	-0.3911	3.5500	-2.9982	-0.2267
6	-1.6862	2.9909	1.6055	-1.6413	2.9545	1.6117	2.1106	-2.2650	1.7570
1	-3.2313	3.4202	-1.5006	-3.1927	3.4379	-1.4741	3.5369	-3.0598	-1.3161
1	-1.2105	2.1036	2.0270	-1.1742	2.0554	2.0184	1.0587	-2.1020	2.0130
1	-3.1058	4.6058	-0.1578	-3.0453	4.6058	-0.1179	3.7160	-3.9877	0.2127
1	-4.1315	3.1883	0.0238	-4.0876	3.2002	0.0517	4.3889	-2.3636	0.0937
1	-2.5528	3.2905	2.1994	-2.4980	3.2610	2.2164	2.6900	-1.3884	2.0845
1	-0.9594	3.8133	1.6443	-0.9013	3.7646	1.6533	2.5133	-3.1333	2.2871

Table S11. DFT optimized geometries for $[(DAB_B)Pt^{IV}(CH_3)_3(acetone)]^+$ **2B** in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	Y	z
6	0.8130	-1.3519	1.5705	0.8092	-1.3685	1.5426	0.8727	-1.4311	1.5461
6	-4.8093	0.1691	1.1737	-4.7951	0.1304	1.1890	-4.6767	0.1693	1.1308
6	3.5563	-1.6906	0.1461	3.5374	-1.6813	0.1248	3.6402	-1.5728	0.1796
6	2.8121	-0.5711	0.5390	2.7952	-0.5652	0.5245	2.8287	-0.5071	0.5617
6	-0.6902	-1.4277	1.5345	-0.6865	-1.4449	1.5042	-0.6221	-1.5376	1.5022
6	-5.4606	-0.5951	0.1972	-5.4410	-0.5972	0.1842	-5.3512	-0.5570	0.1467
6	-3.3717	-1.5483	-0.5318	-3.3501	-1.5081	-0.5811	-3.3087	-1.5998	-0.5649
6	-2.7110	-0.8013	0.4456	-2.6944	-0.7968	0.4237	-2.6290	-0.8897	0.4176
6	4.8252	0.7694	0.6451	4.8071	0.7691	0.6472	4.7304	0.9726	0.6251
6	5.5571	-0.3574	0.2545	5.5366	-0.3536	0.2477	5.5345	-0.1022	0.2367
6	4.9430	-1.5898	-0.0080	4.9222	-1.5813	-0.0266	5.0111	-1.3728	0.0021
6	3.4346	0.6554	0.7741	3.4178	0.6567	0.7712	3.3608	0.7636	0.7694
6	-4.7642	-1.4606	-0.6553	-4.7408	-1.4234	-0.7010	-4.6908	-1.4477	-0.6990
6	-3.4195	0.0565	1.2939	-3.4066	0.0213	1.3043	-3.3008	-0.0068	1.2643
7	1.3851	-0.6600	0.6396	1.3746	-0.6545	0.6251	1.4204	-0.6725	0.6597
7	-1.2806	-0.8597	0.5342	-1.2707	-0.8554	0.5132	-1.2114	-0.9809	0.5018
78	0.0353	0.1988	-0.8951	0.0383	0.2107	-0.8688	0.0691	0.1817	-0.8759
6	-1.4269	0.8257	-2.1960	-1.4051	0.8379	-2.1685	-1.3966	0.7542	-2.1827
6	1.4460	1.1511	-2.0475	1.4469	1.1679	-1.9950	1.4428	1.2435	-1.9575
1	-6.5400	-0.5107	0.0948	-6.5212	-0.5149	0.0849	-6.4277	-0.4217	0.0355
1	6.6360	-0.2738	0.1485	6.6161	-0.2705	0.1433	6.6053	0.0597	0.1078
1	-1.0281	1.3411	-3.0728	-1.0042	1.3605	-3.0411	-1.0282	1.3424	-3.0301
1	-2.1024	1.4947	-1.6524	-2.0927	1.4999	-1.6302	-2.1343	1.3394	-1.6156
1	-2.0049	-0.0385	-2.5324	-1.9784	-0.0251	-2.5186	-1.8970	-0.1407	-2.5709
1	1.1313	1.2792	-3.0854	1.1243	1.3512	-3.0230	1.1123	1.4686	-2.9770
1	2.3718	0.5706	-2.0275	2.3594	0.5655	-2.0171	2.3751	0.6674	-2.0056
1	1.6459	2.1353	-1.6112	1.6833	2.1267	-1.5199	1.6421	2.1819	-1.4227
6	1.5432	-2.0509	2.6845	1.5431	-2.0861	2.6334	1.6135	-2.1583	2.6178
1	1.5002	-3.1387	2.5547	1.5150	-3.1702	2.4735	1.6077	-3.2396	2.4291
1	2.5901	-1.7546	2.7160	2.5869	-1.7771	2.6742	2.6531	-1.8313	2.6732
1	1.0778	-1.8254	3.6481	1.0738	-1.8934	3.6024	1.1377	-2.0032	3.5918
6	-1.4015	-2.1652	2.6360	-1.4003	-2.2034	2.5806	-1.3274	-2.2635	2.5984
1	-1.3438	-1.6070	3.5777	-1.3516	-1.6656	3.5344	-1.2908	-1.6872	3.5320
1	-2.4523	-2.3153	2.3943	-2.4497	-2.3508	2.3277	-2.3760	-2.4337	2.3478
1	-0.9318	-3.1372	2.8109	-0.9290	-3.1780	2.7382	-0.8466	-3.2266	2.7991
6	0.3391	-1.4431	-2.0810	0.3511	-1.4024	-2.0667	0.4825	-1.3688	-2.1295
1	-0.2544	-2.2747	-1.6916	-0.2476	-2.2410	-1.6992	-0.2043	-2.1918	-1.9010
1	0.0462	-1.2342	-3.1104	0.0729	-1.1789	-3.0978	0.3647	-1.0663	-3.1737
1	1.4002	-1.7018	-2.0514	1.4114	-1.6664	-2.0301	1.5173	-1.6847	-1.9541
6	-0.4231	3.2128	0.5164	-0.4369	3.1849	0.5189	-0.7749	3.0211	0.5789
8	-0.2540	1.9913	0.5749	-0.2629	1.9661	0.5891	-0.4208	1.8460	0.6672

6	-0.5750	3.9931	1.7973	-0.6150	3.9677	1.7890	-1.2788	3.7287	1.7956
6	-0.4861	3.9845	-0.7730	-0.4843	3.9461	-0.7703	-0.7372	3.8038	-0.6911
1	-0.3873	3.3561	2.6621	-0.4276	3.3404	2.6607	-1.0631	3.1545	2.6987
1	-0.5005	3.3285	-1.6401	-0.4573	3.2858	-1.6342	-0.5357	3.1729	-1.5580
1	-1.5923	4.3986	1.8565	-1.6401	4.3548	1.8331	-2.3660	3.8516	1.6995
1	0.1040	4.8524	1.8078	0.0467	4.8400	1.8021	-0.8585	4.7373	1.8728
1	0.3854	4.6481	-0.8327	0.3682	4.6349	-0.8089	0.0503	4.5647	-0.6084
1	-1.3679	4.6341	-0.7774	-1.3835	4.5706	-0.8015	-1.6766	4.3510	-0.8299
1	-2.8822	0.6456	2.0315	-2.8716	0.5845	2.0640	-2.7365	0.5521	2.0118
1	-2.8040	-2.2009	-1.1876	-2.7781	-2.1327	-1.2605	-2.7613	-2.2745	-1.2222
1	2.8361	1.5113	1.0708	2.8190	1.5108	1.0735	2.6960	1.5799	1.0507
1	3.0519	-2.6327	-0.0482	3.0310	-2.6208	-0.0797	3.1989	-2.5540	0.0017
6	-5.5940	1.0803	2.0880	-5.5826	0.9940	2.1387	-5.4262	1.1107	2.0247
1	-6.3043	1.6931	1.5241	-6.3273	1.5934	1.6066	-5.9958	1.8434	1.4415
1	-6.1758	0.5017	2.8149	-6.1242	0.3802	2.8675	-6.1495	0.5721	2.6481
1	-4.9382	1.7512	2.6492	-4.9353	1.6749	2.6977	-4.7548	1.6576	2.6947
6	-5.5002	-2.2941	-1.6771	-5.4709	-2.2158	-1.7521	-5.4466	-2.2397	-1.7220
1	-4.8445	-2.5980	-2.4974	-4.8083	-2.5084	-2.5706	-4.8251	-2.4725	-2.5928
1	-5.9021	-3.2069	-1.2213	-5.8933	-3.1331	-1.3254	-5.7903	-3.1937	-1.3034
1	-6.3456	-1.7454	-2.1017	-6.3015	-1.6433	-2.1744	-6.3337	-1.7013	-2.0698
6	5.5102	2.0922	0.8943	5.4907	2.0840	0.9125	5.3377	2.3171	0.8872
1	5.0564	2.6277	1.7337	5.0719	2.5841	1.7910	4.5766	3.1012	0.9486
1	6.5722	1.9567	1.1134	6.5625	1.9510	1.0781	5.8933	2.3203	1.8328
1	5.4376	2.7420	0.0138	5.3715	2.7641	0.0608	6.0471	2.5929	0.0994
6	5.7632	-2.7785	-0.4495	5.7391	-2.7630	-0.4764	5.8949	-2.4944	-0.4525
1	6.6017	-2.9554	0.2318	6.5684	-2.9551	0.2119	6.8867	-2.4327	0.0067
1	5.1627	-3.6907	-0.4914	5.1357	-3.6718	-0.5408	5.4672	-3.4723	-0.2096
1	6.1876	-2.6128	-1.4461	6.1759	-2.5821	-1.4647	6.0401	-2.4623	-1.5393

Table S12. DFT optimized geometries for $[(DAB_B)Pt^{IV}(CH_3)_3]^+$ (**I-1B**) in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	x	y	z	x	Y	z
6	-0.7529	1.7399	0.7812	-0.7498	1.7165	0.8055	0.7387	1.7517	-0.8776
6	4.8148	-0.4763	1.1045	4.7934	-0.5093	1.0887	-4.7804	-0.5986	-0.9778
6	-3.4650	1.1889	-0.7347	-3.4503	1.2049	-0.7032	3.4062	1.2652	0.6421
6	-2.7675	0.5541	0.2995	-2.7507	0.5334	0.3035	2.7362	0.5621	-0.3580
6	0.7563	1.7379	0.7854	0.7522	1.7148	0.8081	-0.7637	1.7423	-0.8763
6	5.5094	0.2429	0.1205	5.4878	0.2307	0.1227	-5.4550	0.1635	-0.0227
6	3.4695	1.2531	-0.6620	3.4515	1.2544	-0.6404	-3.4308	1.2928	0.5944
6	2.7655	0.5425	0.3141	2.7478	0.5227	0.3173	-2.7450	0.5352	-0.3552
6	-4.8209	-0.4073	1.1461	-4.7981	-0.4570	1.1199	4.7802	-0.5309	-1.0186

6	-5.5068	0.2298	0.1066	-5.4863	0.2176	0.1084	5.4402	0.1728	-0.0104
6	-4.8506	1.0271	-0.8419	-4.8342	1.0474	-0.8117	4.7753	1.0701	0.8271
6	-3.4298	-0.2494	1.2269	-3.4088	-0.3030	1.2015	3.4067	-0.3410	-1.1761
6	4.8589	1.1000	-0.7731	4.8391	1.1051	-0.7524	-4.8015	1.1057	0.7733
6	3.4262	-0.3312	1.1835	3.4065	-0.3679	1.1680	-3.4046	-0.4182	-1.1253
7	-1.3356	0.6615	0.3681	-1.3255	0.6419	0.3743	1.3202	0.6743	-0.4745
7	1.3374	0.6496	0.3949	1.3263	0.6296	0.4005	-1.3321	0.6554	-0.4773
78	-0.0086	-0.9832	-0.2960	-0.0084	-0.9600	-0.3061	0.0166	-0.9567	0.2661
6	1.3693	-2.4311	-0.7373	1.3576	-2.3890	-0.7806	-1.3417	-2.3602	0.8455
6	-1.4369	-2.3524	-0.8017	-1.4235	-2.3103	-0.8413	1.4446	-2.2757	0.8603
1	6.5882	0.1276	0.0480	6.5672	0.1178	0.0496	-6.5267	0.0126	0.1121
1	-6.5832	0.0981	0.0284	-6.5634	0.0893	0.0294	6.5095	0.0126	0.1323
1	1.1475	-2.9684	-1.6612	1.1374	-2.9053	-1.7177	-1.1173	-2.8076	1.8186
1	1.3500	-3.1488	0.0947	1.3375	-3.1294	0.0320	-1.3256	-3.1532	0.0834
1	2.3653	-1.9859	-0.8009	2.3573	-1.9486	-0.8340	-2.3376	-1.9010	0.8721
1	-1.1250	-3.0389	-1.5906	-1.1124	-2.9830	-1.6433	1.1336	-2.9293	1.6803
1	-2.3540	-1.8366	-1.0977	-2.3442	-1.7938	-1.1277	2.3474	-1.7207	1.1454
1	-1.6375	-2.9351	0.1093	-1.6256	-2.9142	0.0563	1.6712	-2.8958	-0.0209
6	-1.4714	2.9638	1.2745	-1.4714	2.9217	1.3199	1.4498	2.9734	-1.3507
1	-1.1886	3.8431	0.6860	-1.1927	3.8145	0.7502	1.2113	3.8358	-0.7161
1	-2.5509	2.8398	1.2213	-2.5508	2.7927	1.2634	2.5312	2.8310	-1.3489
1	-1.1915	3.1727	2.3127	-1.1936	3.1104	2.3627	1.1315	3.2322	-2.3670
6	1.4750	2.9699	1.2593	1.4747	2.9305	1.2968	-1.4883	2.9595	-1.3424
1	1.0829	3.2921	2.2284	1.0809	3.2455	2.2677	-1.0861	3.3068	-2.2997
1	2.5451	2.7938	1.3495	2.5437	2.7445	1.3895	-2.5563	2.7674	-1.4551
1	1.3206	3.8010	0.5615	1.3307	3.7707	0.6077	-1.3638	3.7845	-0.6292
6	0.1268	-0.3044	-2.2261	0.1307	-0.2531	-2.2070	-0.1020	-0.1740	2.1455
1	-0.3771	0.6627	-2.2581	-0.3709	0.7164	-2.2252	0.4419	0.7755	2.1169
1	1.1877	-0.2110	-2.4586	1.1922	-0.1576	-2.4393	-1.1647	-0.0291	2.3614
1	-0.3610	-1.0230	-2.8825	-0.3576	-0.9574	-2.8798	0.3550	-0.8705	2.8512
1	-2.9274	1.7935	-1.4596	-2.9142	1.8346	-1.4083	2.8551	1.9504	1.2871
1	-2.8670	-0.7431	2.0142	-2.8429	-0.8251	1.9685	2.8561	-0.8952	-1.9361
1	2.9378	1.9147	-1.3404	2.9192	1.9290	-1.3062	-2.8885	2.0136	1.2073
1	2.8597	-0.8791	1.9307	2.8380	-0.9319	1.9022	-2.8429	-1.0154	-1.8434
6	-5.6276	1.7030	-1.9462	-5.6124	1.7605	-1.8847	5.5235	1.8092	1.8943
1	-4.9654	2.1588	-2.6867	-4.9538	2.2374	-2.6149	4.8522	2.3813	2.5419
1	-6.2758	0.9901	-2.4653	-6.2674	1.0679	-2.4222	6.0955	1.1201	2.5253
1	-6.2737	2.4921	-1.5452	-6.2516	2.5387	-1.4529	6.2430	2.5109	1.4560
6	-5.5553	-1.2363	2.1721	-5.5268	-1.3209	2.1137	5.5319	-1.4629	-1.9188
1	-6.5429	-1.5331	1.8111	-6.5219	-1.5913	1.7527	6.3309	-1.9810	-1.3789
1	-4.9995	-2.1435	2.4278	-4.9781	-2.2444	2.3214	4.8745	-2.2173	-2.3623
1	-5.7001	-0.6711	3.1005	-5.6535	-0.7958	3.0676	6.0037	-0.9145	-2.7433
6	5.6288	1.8300	-1.8477	5.6076	1.8555	-1.8069	-5.5624	1.8933	1.7961

1	6.6381	2.0823	-1.5119	6.6193	2.0938	-1.4681	-6.3716	2.4671	1.3301
1	5.7306	1.2082	-2.7452	5.7029	1.2548	-2.7191	-6.0271	1.2322	2.5365
1	5.1277	2.7552	-2.1456	5.1116	2.7906	-2.0808	-4.9180	2.5963	2.3324
6	5.5555	-1.3840	2.0567	5.5313	-1.4338	2.0189	-5.5196	-1.5813	-1.8333
1	4.8716	-1.9138	2.7243	4.8486	-1.9733	2.6797	-4.8549	-2.3560	-2.2281
1	6.1426	-2.1309	1.5121	6.1131	-2.1728	1.4584	-6.3223	-2.0724	-1.2740
1	6.2562	-0.8145	2.6771	6.2363	-0.8777	2.6462	-5.9848	-1.0803	-2.6911

Table S13. DFT optimized geometries for **TS-B** in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	X	y	z	x	y	z
6	0.7843	1.8377	0.4314	0.7870	1.8217	0.4573	0.7972	1.7850	0.7646
6	-4.8209	0.9036	-1.0031	-4.7838	0.7611	-1.0648	-4.7570	1.1269	-0.8300
6	3.4293	0.1378	1.2855	3.4081	-0.0216	1.2419	3.3956	-0.2841	1.1490
6	2.7658	0.5458	0.1283	2.7509	0.5244	0.1415	2.7495	0.5336	0.2319
6	-0.7081	1.8802	0.4553	-0.6992	1.8687	0.4623	-0.6916	1.8376	0.7919
6	-5.4690	0.2893	0.0751	-5.4442	0.2838	0.0717	-5.3988	0.2013	-0.0045
6	-3.3834	0.0122	1.2491	-3.3744	0.1459	1.2907	-3.3475	-0.2909	1.1400
6	-2.7257	0.6345	0.1842	-2.7055	0.6265	0.1647	-2.6974	0.6335	0.3270
6	4.8450	0.6247	-1.1003	4.8347	0.7696	-1.0506	4.8084	0.9406	-0.9461
6	5.5042	0.2176	0.0657	5.4888	0.2372	0.0640	5.4541	0.1243	-0.0151
6	4.8197	-0.0270	1.2635	4.7984	-0.1641	1.2136	4.7726	-0.4875	1.0371
6	3.4530	0.7849	-1.0610	3.4436	0.9176	-1.0008	3.4351	1.1466	-0.8124
6	-4.7736	-0.1530	1.2087	-4.7630	-0.0217	1.2549	-4.7185	-0.5049	0.9887
6	-3.4311	1.0756	-0.9392	-3.3951	0.9294	-1.0103	-3.3894	1.3416	-0.6550
7	1.3246	0.6839	0.1557	1.3181	0.6644	0.1815	1.3247	0.6854	0.3212
7	-1.2949	0.7493	0.2186	-1.2792	0.7424	0.1949	-1.2831	0.7506	0.4241
78	0.0608	-0.8875	-0.2189	0.0531	-0.8757	-0.2195	0.0439	-0.8156	-0.2953
6	-1.3530	-2.0414	-1.4958	-1.3108	-2.0015	-1.5065	-1.3982	-1.7012	-1.6854
6	1.5545	-2.2409	-0.6300	1.5281	-2.2389	-0.5962	1.5046	-2.0741	-0.9909
1	-6.5463	0.1489	0.0309	-6.5224	0.1450	0.0344	-6.4654	0.0222	-0.1435
1	6.5827	0.0813	0.0393	6.5708	0.1281	0.0360	6.5265	-0.0456	-0.1187
1	-1.3551	-3.0862	-1.7927	-1.2889	-3.0453	-1.8097	-1.3911	-2.6702	-2.1825
1	-0.7177	-1.5151	-2.2273	-0.6628	-1.4672	-2.2278	-0.8362	-1.0175	-2.3513
1	-2.3495	-1.6105	-1.4936	-2.3131	-1.5825	-1.5403	-2.4109	-1.3207	-1.5442
1	1.1702	-3.1806	-1.0380	1.1487	-3.1559	-1.0594	1.1231	-2.7731	-1.7450
1	2.1066	-2.4559	0.2909	2.0280	-2.5029	0.3424	1.9104	-2.6475	-0.1472
1	2.2460	-1.8023	-1.3548	2.2686	-1.7934	-1.2676	2.3118	-1.4793	-1.4337
6	1.5600	3.0852	0.7326	1.5685	3.0547	0.7712	1.5772	2.9553	1.2505
1	1.3767	3.4017	1.7661	1.1942	3.5186	1.6889	1.2792	3.2114	2.2739
1	2.6293	2.9384	0.5992	2.6293	2.8393	0.8869	2.6503	2.7634	1.2348

1	1.2294	3.9043	0.0858	1.4516	3.7936	-0.0305	1.3715	3.8378	0.6317
6	-1.4092	3.1729	0.7583	-1.4060	3.1468	0.7796	-1.3793	3.0817	1.2375
1	-1.2476	3.8974	-0.0483	-1.0695	3.9502	0.1162	-1.2335	3.8888	0.5082
1	-2.4812	3.0231	0.8745	-2.4850	3.0367	0.6800	-2.4522	2.9203	1.3559
1	-1.0107	3.6203	1.6740	-1.1809	3.4626	1.8046	-0.9672	3.4359	2.1884
6	-1.2062	-2.6334	0.3565	-1.2229	-2.5760	0.3358	-1.1473	-2.6393	-0.0003
1	-0.8360	-2.2376	1.3179	-0.8735	-2.1817	1.3094	-0.7545	-2.4497	1.0182
1	-2.2899	-2.6614	0.4193	-2.3089	-2.5911	0.3777	-2.2311	-2.7095	0.0896
1	-0.7689	-3.6130	0.1946	-0.7957	-3.5648	0.1972	-0.7035	-3.5617	-0.3709
1	2.8655	-0.0573	2.1930	2.8381	-0.3259	2.1153	2.8234	-0.7692	1.9394
1	2.9080	1.0844	-1.9516	2.9021	1.3270	-1.8494	2.8930	1.7621	-1.5302
1	-2.8148	-0.3253	2.1107	-2.8147	-0.0874	2.1924	-2.7825	-0.8345	1.8968
1	-2.8971	1.5372	-1.7650	-2.8495	1.2896	-1.8785	-2.8518	2.0339	-1.3031
6	5.5684	-0.4488	2.5052	5.5390	-0.7464	2.3873	5.5038	-1.3342	2.0336
1	4.8891	-0.7929	3.2891	4.8854	-0.8808	3.2525	4.8360	-2.0472	2.5272
1	6.2716	-1.2583	2.2860	5.9629	-1.7244	2.1338	6.3143	-1.8971	1.5597
1	6.1529	0.3842	2.9126	6.3716	-0.1029	2.6887	5.9574	-0.7141	2.8166
6	5.6167	0.9048	-2.3676	5.6036	1.1553	-2.2857	5.5809	1.5780	-2.0606
1	4.9787	0.8331	-3.2525	5.7808	0.2794	-2.9207	4.9289	2.1265	-2.7470
1	6.0446	1.9143	-2.3501	5.0627	1.8916	-2.8861	6.3263	2.2816	-1.6717
1	6.4473	0.2039	-2.4889	6.5809	1.5747	-2.0317	6.1262	0.8264	-2.6423
6	-5.5109	-0.7784	2.3687	-5.5114	-0.5008	2.4698	-5.4420	-1.4660	1.8817
1	-6.0175	-0.0120	2.9668	-6.0197	0.3335	2.9667	-5.8473	-0.9527	2.7623
1	-6.2793	-1.4756	2.0218	-6.2797	-1.2314	2.2002	-6.2855	-1.9350	1.3655
1	-4.8336	-1.3205	3.0337	-4.8440	-0.9630	3.2015	-4.7790	-2.2583	2.2452
6	-5.6034	1.3918	-2.1988	-5.5519	1.1073	-2.3122	-5.5271	1.8790	-1.8722
1	-4.9646	1.5137	-3.0775	-4.9018	1.1510	-3.1897	-4.8658	2.3677	-2.5942
1	-6.4086	0.6980	-2.4565	-6.3403	0.3751	-2.5085	-6.2020	1.2159	-2.4237
1	-6.0679	2.3631	-1.9911	-6.0369	2.0851	-2.2110	-6.1490	2.6571	-1.4134

Table S14. DFT optimized geometries for $[(DAB_B)Pt^{IV}(CH_3)(acetone)]^+$ (**3B**) in Cartesian coordinates.

	B3LYP			B3PW91			M06		
atomic #	x	y	z	X	y	z	x	Y	z
6	1.0475	-2.0434	0.0089	1.0411	-2.0340	0.0601	-1.1277	2.0096	-0.1456
6	-4.6543	-1.4712	0.9643	-4.6486	-1.4031	0.9704	4.5391	1.4939	0.8919
6	3.6208	-0.5555	-1.2022	3.5951	-0.5903	-1.1957	-3.6987	0.5038	-1.1503
6	2.9151	-0.5577	-0.0011	2.8962	-0.5493	0.0061	-2.9501	0.4958	0.0207
6	-0.4276	-2.2103	-0.0440	-0.4282	-2.1972	0.0106	0.3384	2.1984	-0.2454
6	-5.2852	-0.8645	-0.1302	-5.2640	-0.8433	-0.1512	5.1746	0.7014	-0.0664

6	-3.1654	-0.4192	-1.1828	-3.1375	-0.4467	-1.2018	3.0872	0.2537	-1.1658
6	-2.5223	-1.0512	-0.1137	-2.5077	-1.0323	-0.0985	2.4376	1.0493	-0.2214
6	4.9222	-0.0503	1.2431	4.9053	-0.0020	1.2222	-4.8745	-0.1254	1.3198
6	5.6268	-0.0525	0.0311	5.6034	-0.0466	0.0090	-5.6212	-0.1231	0.1408
6	4.9988	-0.2955	-1.1953	4.9715	-0.3313	-1.2037	-5.0557	0.1824	-1.0981
6	3.5460	-0.3028	1.2173	3.5308	-0.2524	1.2111	-3.5146	0.1811	1.2497
6	-4.5626	-0.3416	-1.2108	-4.5294	-0.3681	-1.2471	4.4713	0.0914	-1.1085
6	-3.2588	-1.5694	0.9595	-3.2517	-1.5022	0.9848	3.1565	1.6658	0.8051
7	1.4885	-0.8127	-0.0217	1.4760	-0.8034	-0.0002	-1.5415	0.7780	-0.0505
7	-1.0951	-1.0970	-0.1092	-1.0855	-1.0805	-0.0799	1.0215	1.0995	-0.2446
78	0.1517	0.6622	-0.1288	0.1476	0.6514	-0.1330	-0.1938	-0.6927	-0.1029
6	1.5032	2.2031	-0.1339	1.4901	2.1816	-0.1688	-1.5074	-2.2423	0.0830
1	-6.3706	-0.7946	-0.1394	-6.3491	-0.7713	-0.1743	6.2539	0.5583	-0.0014
1	6.6964	0.1436	0.0443	6.6732	0.1507	0.0107	-6.6817	-0.3735	0.1882
1	1.0089	3.1746	-0.2429	1.0004	3.1524	-0.3075	-1.0148	-3.1966	-0.1354
1	2.1952	2.0791	-0.9736	2.1901	2.0373	-0.9995	-2.3474	-2.1062	-0.6095
1	2.0901	2.2055	0.7910	2.0736	2.2101	0.7587	-1.9051	-2.2668	1.1066
6	1.9342	-3.2507	0.0894	1.9293	-3.2303	0.1651	-2.0347	3.1902	-0.1429
1	1.9243	-3.7931	-0.8638	1.9404	-3.7809	-0.7834	-2.1554	3.5826	-1.1615
1	2.9633	-2.9804	0.3162	2.9535	-2.9492	0.4054	-3.0259	2.9338	0.2348
1	1.5691	-3.9416	0.8552	1.5572	-3.9169	0.9312	-1.6179	3.9989	0.4658
6	-1.0203	-3.5909	-0.0627	-1.0294	-3.5671	0.0197	0.9026	3.5734	-0.3620
1	-0.9558	-4.0641	0.9242	-0.9685	-4.0206	1.0159	0.8435	4.1122	0.5925
1	-2.0689	-3.5650	-0.3563	-2.0786	-3.5380	-0.2743	1.9502	3.5457	-0.6686
1	-0.4712	-4.2300	-0.7601	-0.4858	-4.2248	-0.6649	0.3352	4.1589	-1.0934
6	-1.8449	2.8503	0.4766	-1.8267	2.8210	0.4613	2.2090	-2.3943	0.4662
8	-1.3273	2.0766	-0.3486	-1.3134	2.0556	-0.3726	1.2938	-2.1162	-0.3225
6	-2.9126	3.7835	-0.0054	-2.8784	3.7690	-0.0090	3.2979	-3.2938	0.0045
6	-1.4349	2.8934	1.9171	-1.4195	2.8359	1.8971	2.2811	-1.8338	1.8407
1	-2.9959	3.7539	-1.0916	-2.9635	3.7529	-1.0953	3.1796	-3.5441	-1.0513
1	-1.0447	1.9272	2.2420	-1.0764	1.8486	2.2139	1.2809	-1.5994	2.2198
1	-2.7033	4.8039	0.3337	-2.6554	4.7826	0.3415	3.3033	-4.2113	0.6056
1	-3.8699	3.4936	0.4455	-3.8388	3.4879	0.4402	4.2651	-2.8025	0.1754
1	-2.2595	3.2177	2.5562	-2.2246	3.1976	2.5404	2.8497	-0.8922	1.7834
1	-0.6283	3.6317	2.0183	-0.5735	3.5282	2.0007	2.8141	-2.5016	2.5235
1	-2.7419	-2.0250	1.7991	-2.7423	-1.9212	1.8488	2.6310	2.2472	1.5623
1	-2.5727	-0.0110	-1.9955	-2.5330	-0.0759	-2.0244	2.5034	-0.2336	-1.9461
1	2.9676	-0.3052	2.1363	2.9544	-0.2204	2.1314	-2.8921	0.1681	2.1438
1	3.1009	-0.7453	-2.1368	3.0693	-0.8096	-2.1209	-3.2175	0.7357	-2.1004
6	-5.4643	-1.9955	2.1264	-5.4569	-1.8931	2.1426	5.3278	2.1605	1.9780
1	-6.3097	-2.5977	1.7796	-6.5288	-1.7923	1.9581	6.1529	1.5276	2.3205
1	-4.8595	-2.6145	2.7941	-5.2520	-2.9481	2.3534	5.7713	3.0970	1.6184
1	-5.8781	-1.1728	2.7212	-5.2193	-1.3303	3.0521	4.7034	2.4060	2.8427

6	-5.2760	0.2715	-2.3925	-5.2325	0.1968	-2.4523	5.1903	-0.7152	-2.1472
1	-4.6328	0.9715	-2.9328	-4.5507	0.7689	-3.0867	4.5202	-1.4224	-2.6474
1	-5.5863	-0.5025	-3.1045	-5.6575	-0.6062	-3.0654	5.6114	-0.0644	-2.9231
1	-6.1796	0.8039	-2.0819	-6.0605	0.8506	-2.1618	6.0260	-1.2762	-1.7147
6	5.6373	0.2189	2.5457	5.6260	0.3024	2.5082	-5.5246	-0.4353	2.6338
1	4.9555	0.1686	3.3984	4.9346	0.3810	3.3508	-4.7884	-0.7080	3.3963
1	6.4400	-0.5074	2.7128	6.3550	-0.4805	2.7448	-6.0835	0.4305	3.0097
1	6.0986	1.2124	2.5425	6.1783	1.2449	2.4359	-6.2383	-1.2604	2.5393
6	5.7783	-0.2537	-2.4881	5.7406	-0.3335	-2.4975	-5.8860	0.1449	-2.3449
1	6.8105	-0.5832	-2.3418	6.7975	-0.5581	-2.3334	-6.8587	0.6242	-2.1905
1	5.3231	-0.8872	-3.2544	5.3418	-1.0678	-3.2032	-5.3881	0.6464	-3.1804
1	5.8153	0.7671	-2.8871	5.6855	0.6483	-2.9825	-6.0835	-0.8892	-2.6518

Table S15. DFT optimized geometries for $[(DAB_C)Pt^{IV}(CH_3)(C_2H_6)]^+$ (**I-2**) in Cartesian coordinates. Determined using the hybrid exchange and correlation functional of B3LYP.

	I-2C			**I-2B**		
atomic #	x	y	z	x	Y	z
6	-0.5849	1.9757	0.1957	0.6120	1.9718	0.0553
6	4.8281	-0.1040	1.2571	-4.8806	0.1451	-1.1879
6	-3.2971	0.7271	-1.2652	3.2614	0.2436	1.2458
6	-2.6500	0.7724	-0.0152	2.6519	0.7384	0.0893
6	0.8987	1.8505	0.2171	-0.8740	1.8831	0.0190
6	5.5383	-0.0547	0.0590	-5.5538	0.1555	0.0396
6	3.4999	0.4703	-1.1603	-3.4955	0.5037	1.2391
6	2.8161	0.4242	0.0682	-2.8197	0.5008	0.0182
6	-4.7330	0.4876	1.1441	4.8009	0.9385	-1.0093
6	-5.4022	0.4503	-0.0777	5.4009	0.4552	0.1600
6	-4.6877	0.5697	-1.2682	4.6540	0.1136	1.2965
6	-3.3436	0.6494	1.2048	3.4070	1.0836	-1.0350
6	4.8779	0.2286	-1.1351	-4.8842	0.3275	1.2587
6	3.4488	0.1301	1.2897	-3.4898	0.3193	-1.1901
7	-1.2123	0.8590	0.0069	1.2212	0.8274	0.0526
7	1.3830	0.6462	0.0696	-1.3812	0.6802	0.0122
78	0.0717	-0.8467	-0.1816	-0.1150	-0.8702	-0.0266
6	1.4088	-2.3936	-0.3055	-1.5749	-2.3105	-0.0467
6	-2.2165	-3.2590	0.9940	2.9513	-2.8326	-0.5708
1	5.3436	-0.3317	2.1854	-6.6331	0.0227	0.0475
1	6.6073	-0.2421	0.0552	6.4817	0.3383	0.1864
1	-5.2902	0.3903	2.0714	-2.1003	-2.2869	-1.0082
1	-6.4801	0.3252	-0.1021	-2.3002	-2.1106	0.7469
1	-5.2101	0.5412	-2.2200	-1.1632	-3.3134	0.1025

1	5.4327	0.2594	-2.0681	3.2547	-3.5857	-1.3046
1	1.1513	-3.1533	0.4441	3.3846	-3.1086	0.3935
1	2.4400	-2.0807	-0.1403	3.3709	-1.8732	-0.8769
1	1.3406	-2.8518	-1.3013	1.2772	3.3156	0.1291
1	-2.6499	-4.2643	0.9956	0.7955	3.9415	0.8859
1	-2.9972	-2.5581	1.3001	2.3348	3.2174	0.3692
1	-1.4162	-3.2393	1.7380	1.1924	3.8443	-0.8276
6	-1.2342	3.3150	0.3813	-1.6951	3.1372	0.0104
1	-0.8530	4.0349	-0.3504	-1.2983	3.8438	-0.7244
1	-2.3156	3.2412	0.2717	-2.7399	2.9353	-0.2149
1	-1.0102	3.7199	1.3747	-1.6421	3.6287	0.9895
6	1.7448	3.0736	0.3983	1.4246	-2.7979	-0.5118
1	1.4616	3.5961	1.3183	1.1412	-2.1403	0.3948
1	2.8046	2.8317	0.4393	0.9907	-2.4934	-1.4696
1	1.5746	3.7735	-0.4279	0.9796	-3.7566	-0.2386
6	-2.5285	0.8686	-2.5573	2.9100	1.4429	-1.9317
1	-1.6873	0.1677	-2.6118	2.6504	-0.0239	2.1032
1	-3.1790	0.6846	-3.4149	-2.9350	0.3146	-2.1236
1	-2.1109	1.8762	-2.6737	-2.9434	0.6345	2.1651
6	-2.6278	0.6874	2.5349	5.6375	1.3207	-2.2070
1	-3.3021	0.3919	3.3414	6.0554	2.3273	-2.0859
1	-1.7636	0.0145	2.5534	6.4797	0.6356	-2.3381
1	-2.2616	1.6933	2.7745	5.0489	1.3175	-3.1283
6	2.7868	0.7562	-2.4593	5.3401	-0.3716	2.5509
1	3.4824	0.6980	-3.2988	4.6401	-0.8664	3.2291
1	1.9786	0.0380	-2.6391	6.1445	-1.0751	2.3164
1	2.3388	1.7569	-2.4746	5.7926	0.4650	3.0961
6	2.6791	0.0601	2.5857	-5.6306	-0.0755	-2.4796
1	1.8481	-0.6515	2.5195	-5.0744	0.3060	-3.3399
1	3.3309	-0.2560	3.4025	-5.8063	-1.1446	-2.6487
1	2.2516	1.0306	2.8652	-6.6083	0.4142	-2.4606
6	-1.6997	-2.9436	-0.4027	-5.6466	0.3213	2.5621
1	-1.4177	-1.8334	-0.5109	-6.4396	1.0764	2.5592
1	-0.8778	-3.5789	-0.7232	-6.1265	-0.6490	2.7300
1	-2.4862	-2.9703	-1.1640	-4.9922	0.5221	3.4139

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