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Preparation and characterization of terdentate [C,N,N] acetophenone and acetylpyridine hydrazone platinacycles. A DFT insight into the reaction mechanism

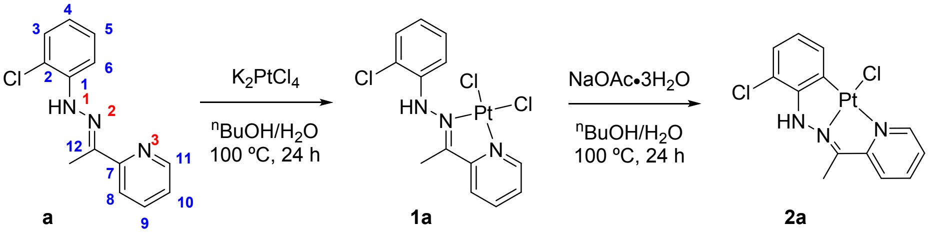
Ismael Marcos,[a] Vicente Ojea,[a] Digna Vázquez-García,[a]* Jesús J. Fernández,[a] Alberto Fernández,[a] Margarita López-Torres,[a] Jorge Lado[a] and José M. Vila.[b]*

[a] Departamento de Química & Centro de Investigaciones Científicas Avanzadas (CICA), Universidade da Coruña.
E-15008 La Coruña, Spain.
Fax: +34/981-167065
E-mail: alberto.fernandez@udc.es
[b] Departamento de Química Inorgánica, Universidad de Santiago de Compostela
E-15782 Santiago de Compostela, Spain
Fax: +34/981-595012
E-mail: qideport@usc.es

Supplementary Information

1. Characterization discussion

Characterization of a derivatives



Scheme S1: preparation of **a** derivatives with labelling scheme.

In the ^{1}H NMR spectrum of **1a** four signals in the 7.50-6.87 ppm range were assigned to the H3-H6 proton resonances (see labeling at scheme 1), being the H6 signal absent in the spectrum of **2a**, as a result of metallation at C6. Metallation was also supported by the presence of satellites due to the ^{195}Pt-H5 coupling [(^3J(H5Pt) = 18.0 Hz]. In the NMR spectrum of **1a** the resonance assigned to the -C=N(H)N- proton appeared at 8.75 ppm, slightly high-field shifted, as compared to the uncoordinated ligand **a**, whilst in the NMR spectrum of **2a** this resonance was significantly shifted towards high frequency (10.16 ppm), as was previously observed for the Pd(II) analogous,[1] and coupled to the ^{195}Pt nucleus. A band assigned to the ν (N-H) vibration at ca. 3200 cm−1 in the IR spectra of **1a** and **2a** confirmed the presence of the NH- protons. The IR spectra also showed the low-frequency shift of the ν(C=N) stretch, as compared to the free ligand, indicative of coordination to the nitrogen atom.[2] The low conductivity shown by the solutions of **1a** and **2a** in dry nitromethane as well as the presence of clusters of peaks at 533 $[(L)PtCl_2Na]^+$ and 476 $[(L)PtCl]^+$ (**1a**) and 498 amu $[(L-H)PtClNa]^+$ (**2a**) in their mass FAB spectra were in agreement with the mononuclear formulation proposed for these complexes.

Metallation of the phenyl ring was also made clear by the low field shift of the C6, C=N, and C1 carbon resonances in the ^{13}C-{^{1}H} NMR spectrum of **2a**.[3]

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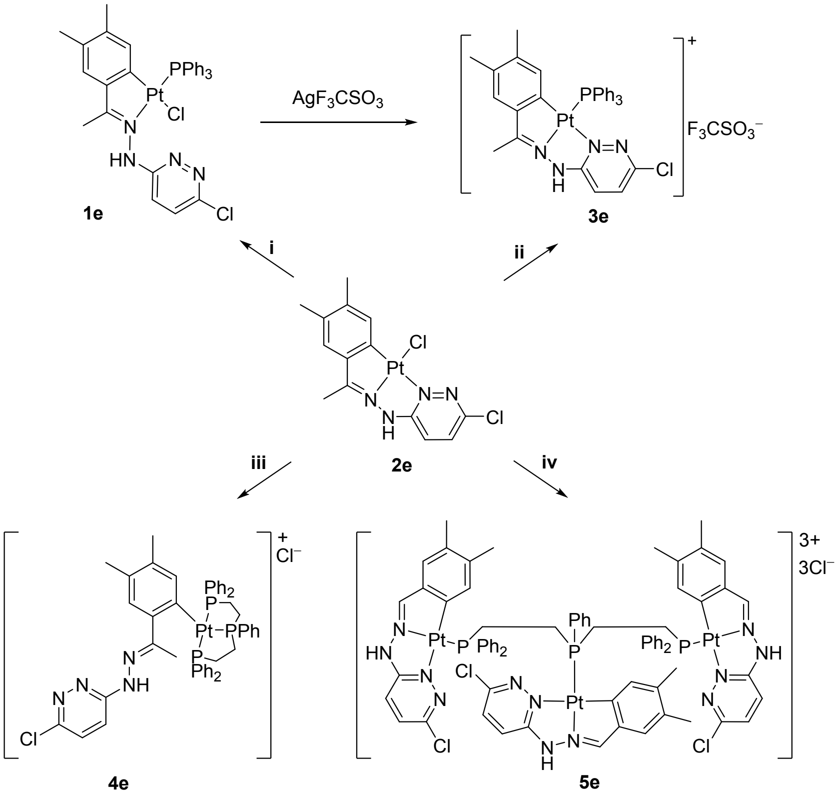
Characterization of e derivatives



Scheme S2. **i**) PPh_3 (acetone, 1:1 molar ratio), **ii**) 1: $AgCF_3SO_3$, 2: PPh_3 (acetone, 1:1 molar ratio), **iii**) triphos (acetone, 1:1 molar ratio), **iv**) triphos (acetone, 3:1 molar ratio).

The low solubility of **2e** precluded its characterizations in solution, however, the structure of the derivatives **1e** and **3e**-**5e**, *vide infra*, was in agreement with the structure proposed. Moreover, recrystallization of **2e** from dimethyl sulfoxide gave crystals of the new complex **2e-dmso** with the chloride ligand replaced by a dimethyl sulfoxide molecule and deprotonation of the hydrazinic nitrogen atom.

The ^{1}H NMR spectrum of **1e** showed a broad singlet at low field due to the NH proton and a signal assigned to H5 at 5.63 ppm [^{4}J(H5P) = 51.6 Hz] upfield shifted due to shielding by the phosphine phenyl rings, 1 confirming phosphine coordination. The ^{31}P-{^{1}H} NMR spectrum showed a singlet resonance at 23.6 ppm with ^{195}Pt satellites nucleus (^{1}J(PtP)= 2075.8 Hz) in accordance with a *trans* phosphorus-to-nitrogen geometry.[4] The conductivity measurement carried out in dry acetonitrile were in agreement with a neutral formulation. The FAB mass spectrum showed the peaks corresponding to the fragment $[(L-H)PtPPh_3]^+$ after the loss of the chlorine ligand.

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The IR and NMR spectra of **3e** were similar to those of **1e**, albeit the NH resonance at δ 11.84 ppm that showed coupling to the ^{31}P and ^{195}Pt nuclei (^{3}J(NHPt)=16.5 Hz, ^{3}J(NHP)= 5.4 Hz). Also, conductivity measurements in dry acetonitrile were in agreement with the 1:1 electrolyte nature of **3e**.

The FAB-mass spectrum of **4e** showed a set of peaks centred at 1002 amu assigned to the [(L-H)Pt(trifos)]$^{+}$ fragment. A broad resonance at δ = 86.7 [^{1}J(PtP) = 859.2 Hz] was assigned to the central ^{31}P nucleus, *trans* to the metallated carbon atom, at 37.1 [^{1}J(PtP) = 1631.1 Hz] was assigned to the two equivalent mutually *trans* phosphorus nuclei 4 The C(5)*H* was a doublet by coupling to the central ^{31}P nucleus [$^{3}J(H_5Pt)$= 16.3, $^{4}J(H_5P)$= 6.3 Hz], no coupling was observed to the terminal phosphorus nuclei. These data are in accordance with a disposition in which the metallated ring is nearly perpendicular to the plane defined by the three phosphorus atoms.[5,6,1] The NH resonance at δ = 10.62 ppm, showed no ^{195}Pt coupling indicating the cleavage of the Pt-N=C bond. The conductivity data in acetonitrile solution were in agreement with a 1:1 electrolyte formulation.

Treatment of **2e** with $(Ph_2PCH_2CH_2)_2PPh$, in a 3:1 molar ratio, gave a green solid, sparingly soluble in most of the common solvents, which could not be satisfactorily characterized. The scarce spectroscopic data revealed that the result was a mixture of **5e** and other unidentified compounds. In the ^{31}P-{^{1}H} NMR spectrum two low intensity resonances at 28.0 and 24.1 ppm were assigned to the non-equivalent central and terminal phosphorus, respectively. Fortunately, a small number of crystals of **5e** suitable for X-ray diffraction were grown from a chloroform solution of this complex.

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2. General methods and complete experimental data.

General Methods

Solvents were purified by standard methods.[7] Reagents were purchased from Sigma-Aldrich and Panreac. All reactions were carried out under argon atmosphere using standard Schlenk techniques. Chemicals were reagent grade. Microanalyses were carried out using a Carlo Erba Elemental Analyser, Model 1108. IR spectra were recorded as KBr discs on a Satellite FTIR. NMR spectra were obtained as $CDCl_3$ or dmso-d^6 solutions and referenced to $SiMe_4$ (^1H, ^{13}C-{^1H}) and were recorded on Bruker Advance 300 and 500F spectrometers. All chemical shifts were reported downfield from standards. The ESI mass spectra were recorded using a QSTAR Elite spectrometer using dichloromethane/acetonitrile or dichloromethane/ethanol as solvents. The FAB mass spectra were recorded using a FISONS Quatro mass spectrometer with a Cs ion gun, 3-nitrobenzyl alcohol was used as the matrix. The ESI mass spectra were recorded using a QSTAR Elite spectrometer using dichloromethane/acetonitrile or dichloromethane/ethanol as solvents. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10^{-3} mol dm^{-3} solutions in acetonitrile, nitrobenzene or nitromethane.

Syntheses

Preparation of 2-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$ (a): A mixture of 2-chlorophenylhydrazine hydrochloride (1.14 g, 9.43 mmol) and 2-acetylpirydine (1.02 g, 9.43 mmol) in 50 cm^3 of ethanol was stirred for 24 h at room temperature (r.t.). The yellow precipitate formed was filtered off and dried in air. Yield: 78%. Anal. found: C, 63.4; H, 4.7; N, 17.2; $C_{13}H_{12}N_3Cl$ requires: C, 63.5; H, 4.9; N, 17.1. IR: ν_{max}/cm^{-1} 1609s (C=N), 3265m (N-H). ^1H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 8.91 (s, 1H, NH), 8.74 (d, 1H, H_{11}, $^3J(H_{11}H_{10})$= 5.4), 8.32 (m, 2H, H_9/H_{10}), 7.99 (dd, 1H, H_8, $^3J(H_8H_9)$= 8.2, $^4J(H_8H_{10})$= 1.3), 7.73 (m, 1H, H_3), 7.44 (dd, 1H, H_6, $^3J(H_6H_5)$= 8.0, $^4J(H_6H_4)$= 1.4), 7.35 (td, 1H, H_5, $^3J(H_5H_6)$=7.7, $^4J(H_5H_3)$= 1.4), 6.98 (td, 1H, H_4, $^3J(H_4H_5)$= 7.7, $^4J(H_4H_6)$= 1.4), 2.47 (s, 3H, Me). ^{13}C NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 151.2 (C_7), 144.9 (C_{11}), 143.3 (C=N), 140.5 (C_1), 129.9 (C_9), 128.6 (C_3/ C_5), 124.9 (C_{10}), 122.9, 122.6 (C_4/C_8), 119.1 (C_2), 116.9 (C_6), 11.7 (Me). Specific molar conductivity: Λ_m = 43.7 S cm^2 mol^{-1} (in nitromethane).

Preparation of $C_6H_5N(H)N{=}CMe(C_5H_4N)$ (b): A mixture of phenylhydrazine (1.02 g, 9.43 mmol) and 2-acetylpyridine (1.14 g, 9.43 mmol) and 0.1 cm^3 of acetic acid in 50 cm^3 of ethanol was stirred under reflux for 24 h. The solvent was removed in vacuo, and the resulting solid was filtered off, triturated with Et_2O and dried in vacuo, giving the desired product as a yellow solid. Yield: 62%. Anal. found: C, 73.6; H, 6.4; N, 19.8; $C_{13}H_{13}N_3$ requires C, 73.9; H, 6.2; N, 19.9. IR: ν_{max}/cm^{-1} 1604m (C=N), 3205m (N-H). ^1H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 9.49 (s, 1H, NH), 8.53 (m, 1H, H_{11}, $^3J(H_{11}H_{10})$= 4.9), 8.12 (m, 1H, H_8, $^3J(H_8H_9)$= 8.2, $^4J(H_8H_{10})$= 1.0), 7.76 (m, 1H, ^3J(HH)= 7.8), 7.27 (m, 5H), 6.80 (m, 1H, ^3J(HH)= 7.04), 2.36 (s, 3H, Me). ^{13}C NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 156.68 (C_7), 148.74 (C_{11}), 146.00 (C=N), 141.83 (C_1), 136.55 (C_9), 129.41 (C_3/C_5), 122.67 (C_{10}), 119.86, 119.65 (C_4/C_8), 113.49 (C_2/C_6), 11.50 (Me). Specific molar conductivity: Λ_m = 22.6 S cm^2 mol^{-1} (in nitromethane).

Compounds **c** and **d** were obtained following a similar procedure to the one used in the synthesis of **a**, as yellow solids.

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[7] D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, 4th ed., Butterwort-Heinemann, 1996.

3-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$ (c): Yield: 90%. Anal. found: C, 63.2; H, 4.6; N, 17.1; $C_{13}H_{12}N_3Cl$ requires C, 63.5; H, 4.9; N, 17.1. IR: ν_{max}/cm^{-1} 1590s (C=N), 3037m (N-H). ^1H NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 10.44 (s, 1H, NH), 8.71 (m, 1H, H_{11}), 8.39 (t, 1H, H_9, $^3J(H_8H_9)$= 8.1), 8.25 (d, 1H, H_8, $^3J(H_8H_9)$= 8.1), 7.74 (t, 1H, H_{10}, $^3J(H_9H_{10})$= 7.9), 7.65 (s, br, 1H, H_2), 7.48 (m, 1H, H_4), 7.29 (t, 1H, H_5, $^3J(H_4H_5)$= 8.1), 6.91 (dd, 1H, H_6, $^3J(H_5H_6)$= 8.1, $^4J(H_4H_6)$= 1.2) 2.41 (s, 3H, Me). ^{13}C NMR (126 MHz, DMSO-d^6, δ ppm, J Hz): δ = 150.4 (C=N), 145.8 (C_1), 144.2 (C_9), 143.7 (C_{11}), 135.6 (C_7), 133.8 (C_3), 130.6 (C_5), 124.0 (C_{10}), 122.6 (C_8), 120.3 (C_6), 113.4 (C_2), 112.7 (C_4), 18.53 (Me). MS-FAB: m/z = 246.1 ((L)H)$^+$.

2,4-Cl-$C_6H_3N(H)N{=}CMe(C_5H_4N)$ (d): Yield: 88%. Anal. found: C, 53.2; H, 4.6; N, 16.4; $C_{12}H_{11}N_3Cl_2$ requires C, 53.7; H, 4.1; N, 15.6. IR: ν_{max}/cm^{-1} 1605s (C=N), 3070m (N-H). ^1H NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 8.99 (s, 1H, NH), 8.75 (dd, 1H, H_{11}, $^3J(H_{10}H_{11})$= 5.7, $^4J(H_9H_{11})$= 1.6), 8.31 (td, 1H, H_9, $^3J(H_8H_9)$= 8.0, $^4J(H_9H_{11})$= 1.6), 8.32 (d, 1H, H_8, $^3J(H_8H_9)$= 8.0), 8.06 (d, 1H, H_6, $^3J(H_5H_6)$= 8.8), 7.80 (m, 1H, H_{10}), 7.59 (d, 1H, H_3, $^4J(H_3H_5)$= 2.3), 7.40 (dd, 1H, H_5, $^3J(H_5H_6)$= 8.8, $^4J(H_3H_5)$= 2.3), 2.46 (s, 3H, Me). ^{13}C NMR (126 MHz, DMSO-d^6, δ ppm, J Hz): δ = 150.4 (C_7), 144.5 (C_{11}), 144.3 (C_9), 140.9 (C=N), 139.8 (C_1), 129.2(C_3), 128.6 (C_5), 125.6 (C_4), 125.2 (C_{10}), 123.4 (C_8), 119.8 (C_2), 118.2 (C_6), 22.3 (Me). MS-FAB: m/z = 280.0 ((L)H)$^+$, 244.0 ((L-Cl))$^+$.

Preparation of 3,4-Me_2-$C_6H_3C(Me){=}NN(H)$(4'-Cl-$C_4H_2N_2$) (e): A mixture of 3,4-dimethyl acetophenone (0.50 g, 3.45 mmol), 0.50 mL of 3-chloro-6-hydrazinopyridazine (3.45 mmol) and 0.1 cm^3 of acetic acid in 50 cm^3 of ethanol was stirred for 48 h to room temperature . The grey precipitate formed was filtered off and dried in air. Yield: 47%. Anal. found: C, 61.3; H, 5.4; N, 20.3; $C_{14}H_{15}N_4Cl$ requires C, 61.2; H, 5.5; N, 20.4. IR: ν_{max}/cm^{-1} 1589s (C=N), 3181w (N-H). ^1H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 10.56 (s, 1H, NH), 7.66, 7.65 (s, 2H, H_8/H_9), 7.60 (s, 1H, H_2), 7.53 (d, 1H, H_6, $^3J(H_6H_5)$= 7.9), 7.14 (d, 1H, H_5, $^3J(H_6H_5)$= 7.9), 2.31 (s, 3H, Me(C=N)), 2.26, 2.23 (s, 3H, Me_a/Me_b). ^{13}C NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 164.89 (s, C=N), 152.70, 152.23 (s, C_7/C_{10}), 142.11, 141.25, 141.12 (s, C_1/C_3/C_4), 135.10, 134.63, 131.99, 128.52(s, C_2/C_5/C_6/C_9), 121.58 (s, C_8), 24.73, 24.38 (s, Me_a/Me_b), 18.87 (s, Me(C=N)). Specific molar conductivity: Λ_m = 17.2 S cm^2 mol^{-1} (in nitromethane).

Preparation of (Pt{2-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$}($Cl_2$)) (1a):

Method 1: A pressure tube containing 2-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$ (ligand **a**) (1.00 g, 4.07 mmol), potassium tetrachloroplatinate (II) (1.40 g, 3.39 mmol) and 0.1 cm^3 of water in 50 cm^3 of 1-buthanol, was sealed under argon. The resulting mixture was stirred for 24 h at 100°C. After cooling to room temperature the orange precipitate formed was filtered off, triturated with Et_2O and dried in vacuo. Yield 93%.

Method 2: To a stirred solution of potassium tetrachloroplatinate (100 mg, 0.241 mmol) in water (2.5 cm^3) was added ethanol (13.5 cm^3). The fine red suspension of potassium tetrachloroplatinate obtained was treated with 2-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$ (ligand **a**) (67 mg, 0.274 mmol). The mixture was stirred under argon for 24 h at 60°. After cooling to room temperature the ochre precipitate formed was filtered off and dried in air. Yield 56%.

Method 3: A pressure tube containing 2-Cl-$C_6H_4N(H)N{=}CMe(C_5H_4N)$ (ligand **a**) (42 mg, 0.175 mmol), (Pt(η^3-allyl)(μ-Cl))$_2$ (50 mg, 0.088 mmol) and 50 cm^3 of dry toluene was sealed under argon. The resulting mixture was stirred at 60 °C for 24h. After cooling to room temperature the ochre precipitate formed was filtered off, triturated with Et_2O and dried in vacuo. Yield 66%. Anal. found: C, 30.4; H, 2.5; N, 8.7; $C_{13}H_{12}N_3Cl_3Pt$ requires C, 30.5; H, 2.4; N, 8.2. IR: ν_{max}/cm^{-1} 1588m (C=N), 3255sh (N-H). ^1H NMR

(300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 9.41 (dd, 1H, H$_{11}$, ^3J(H$_{11}$H$_{10}$)= 5.8, ^4J(H$_{11}$H$_9$)= 0.9), 8.73 (s, 1H, NH), 8.45 (td, 1H, H$_9$, ^3J(H$_9$H$_{10}$)= 7.9, ^4J(H$_9$H$_{11}$)= 1.5), 8.26 (dd, 1H, H$_8$, ^3J(H$_8$H$_9$)= 8.0, ^4J(H$_8$H$_{10}$)= 0.8), 7.97(m, 1H, H$_{10}$), 7.50 (dd, 1H, H$_3$, ^3J(H$_3$H$_4$)= 7.8, ^4J(H$_3$H$_5$)= 1.4), 7.26 (td, 1H, H$_5$, ^3J(H$_5$H$_6$)= 7.8, ^4J(H$_5$H$_3$)= 1.4), 7.07 (td, 1H, H$_4$, ^3J(H$_4$H$_5$)= 7.8, ^4J(H$_4$H$_6$)= 1.4), 6.87 (m, 1H, H$_6$), 2.30 (s, 3H, Me). ^{13}C NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 176.8 (s, C=N), 156.6 (s, C$_7$), 148.9 (s, C$_{11}$), 141.0 (s, C$_9$), 140.3 (s, C$_1$), 130.4, 129.8, 129.2, 128.3, 123.8 (s, C$_3$/ C$_4$/ C$_5$/C$_8$/ C$_{10}$), 120.8 (s, C$_2$), 115.5 (s, C$_6$), 16.9 (s, Me). MS-FAB: m/z = 532.9 ((L)PtCl$_2$Na)$^+$, 498.0 ((L)PtClNa)$^+$, 476.0 ((L)PtCl)$^+$, 440.0 ((L)Pt)$^+$. Specific molar conductivity: Λ_m = 22.9 S cm^2 mol^{-1} (in nitromethane).

(Pt{C$_6$H$_5$N(H)N=CMe(C$_5$H$_4$N)}(Cl$_2$)) (1b): The reaction of ligand **b** and potassium tetrachloroplatinate for 2h under similar conditions (**method 1**) yielded a mixture of the cyclometallated complex, **2b**, and the non-cyclometallated compound, **1b**. **1b** could not be isolated from the mixture, however it was characterized by NMR:^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 9.42 (dd, 1H, H$_{11}$, ^3J(H$_{11}$H$_{10}$)= 5.8, ^4J(H$_{11}$H$_9$)= 1.0), 9.03 (s, 1H, NH), 8.43 (td, 1H, H$_9$, ^3J(H$_9$H$_{10}$)= 8.0, ^4J(H$_9$H$_{11}$)= 1.4), 8.21 (d, 1H, H$_8$, ^3J(H$_8$H$_9$)= 8.0), 7.94 (m, 1H, H$_{10}$, ^3J(H$_{10}$H$_9$)= 7.4, ^3J(H$_{10}$H$_{11}$)= 5.8, ^4J(H$_{10}$H$_8$)= 1.5), 7.30, 6.92 (m, 5H).

(Pt{2,4-Cl-C$_6$H$_3$N(H)N=CMe(C$_5$H$_4$N)}(Cl$_2$)) (1d): Compound **1d** was prepared following a similar procedure to that used for **1a** as an orange solid (**Method 1**). Yield: 48%. Anal. found: C, 28.9; H, 2.2; N, 7.6; C$_{13}$H$_{11}$N$_3$Cl$_4$Pt requires C, 28.6; H, 2.0; N, 7.7. IR: ν_{max}/cm^{-1} 1586w (C=N), 3266m (N-H). ^{1}H NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 9.44 (dd, 1H, H$_{11}$, ^3J(H$_{10}$H$_{11}$)= 8.1, ^4J(H$_9$H$_{11}$)= 1.4), 8.44 (s, 1H, NH), 8.47 (td, 1H, H$_9$, ^3J(H$_8$H$_9$)= 7.8, ^4J(H$_9$H$_{10}$)= 1.5), 8.30 (dd, 1H, H$_8$, ^3J(H$_8$H$_9$)= 8.1, ^4J(H$_8$H$_{10}$)= 1.4), 7.99 (m, 1H, H$_{10}$), 7.65 (d, 1H, H$_3$, ^3J(H$_3$H$_5$)= 2.3), 7.30 (dd, 1H, H$_5$, ^3J(H$_5$H$_6$)= 8.8, ^4J(H$_3$H$_5$)= 2.4), 6.95 (d, 1H, H$_6$, ^3J(H$_5$H$_6$)= 8.8), 2.34 (s, 3H, Me). ^{13}C NMR (126 MHz, DMSO-d^6, δ ppm, J Hz): δ = 178.1 (C=N), 156.0 (C$_7$), 148.5 (C$_{11}$), 140.4 (C$_9$), 139.8 (C$_4$), 129.4(C$_{10}$), 129.1 (C$_8$), 128.9 (C$_3$), 127.6 (C$_5$), 125.8 (C$_1$), 120.7 (C$_2$), 116.2 (C$_6$), 16.2 (Me). MS-FAB: m/z = 508.9 ((L)PtCl$_2$)$^+$.

Preparation of (Pt{2-Cl-C$_6$H$_3$N(H)N=CMe(C$_5$H$_4$N)}(Cl)) (2a): A pressure tube containing (Pt{2-Cl-C$_6$H$_4$N(H)N=CMe(C$_5$H$_4$N)}(Cl$_2$)) (**1a**) (100 mg, 0.195 mmol), sodium acetate trihydrate (26 mg, 0.195 mmol) and 50 cm^3 of 1-buthanol was sealed under argon. The resulting mixture was stirred for 24 h at 100°C. After cooling to room temperature the brown precipitate formed was filtered off, triturated with Et$_2$O and dried in vacuo. Yield 99%. Anal. found: C, 32.6; H, 2.4; N; 8.6; C$_{13}$H$_{11}$N$_3$Cl$_2$Pt requires C, 32.8; H, 2.3; N, 8.8. IR: ν_{max}/cm^{-1} 1596m (C=N), 3271w (N-H). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ= 10,16 (s, 1H, NH, ^3J(NHPt)= 33.2), 8.59 (dd, 1H, H$_{11}$, ^3J(H$_{11}$H$_{10}$)= 4.9, ^4J(H$_{11}$H$_9$)= 1.6), 8.14 (dt, 1H, H$_9$, ^3J(H$_9$H$_{10}$)= 7.9, ^4J(H$_9$H$_{11}$)= 1.6), 7.78 (m, 2H, H$_8$/H$_{10}$), 7.04 (dd, 1H, H$_5$, ^3J(H$_5$Pt)= 18.0, ^3J(H$_5$H$_4$)= 7.7, ^4J(H$_5$H$_3$)= 1.3), 6,93 (dd, 1H, H$_3$, ^3J(H$_3$H$_4$)= 7.7, ^4J(H$_3$H$_5$)= 1.3), 6.67 (t, 1H, H$_4$, ^3J(H$_4$H$_3$)= 7.7), 2.32 (s, 3H, Me). ^{13}C NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 160.21 (s, C=N), 153.94, 152.68 (s, C$_1$/C$_7$), 148.04 (s, C$_{11}$), 141.31 (s, C$_9$), 132.29 (s, C$_4$), 128.12, 125.44, 125.31 (s, C$_3$/C$_8$/C$_{10}$), 127.43 (s, C$_6$), 122.15 (s, C$_5$, ^2J(C$_5$Pt)= 28.5), 112.54 (s, C$_2$), 14.20 (s, Me). MS-FAB: m/z = 498.1 ((L-H)PtClNa)$^+$. Specific molar conductivity: Λ_m = 0.37 S cm^2 mol^{-1} (in nitrobenzene).

(Pt{C$_6$H$_4$N(H)N=CMe(C$_5$H$_4$N)}(Cl)) (2b): Compound **2b** was obtained as an orange solid following similar methods to those used for the preparation of **1a: Method 1** (Yield 91%) or **Method 3** (Yield 75%). Anal. found: C, 35.6; H, 2.6; N, 9.5; C$_{13}$H$_{12}$N$_3$ClPt requires C, 35.4; H, 2.7; N, 9.5. IR: ν_{max}/cm^{-1} 1594w (C=N), 3201w (N-H). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 10.94 (s, 1H, NH, ^3J(NHPt)= 42.3), 8.50 (dd, 1H, H$_{11}$, ^3J(H$_{11}$H$_{10}$)= 5.6, ^4J(H$_{11}$H$_9$)= 1.8), 8.06 (td, 1H, H$_9$, ^3J(H$_9$H$_{10}$)= 7.9, ^4J(H$_9$H$_{11}$)= 1.8), 7.64 (m, 2H, H$_8$/H$_{10}$), 7.03 (dd, 1H, H$_5$, ^4J(H$_5$Pt)= 21.4, ^3J(H$_5$H$_4$)= 7.5, ^4J(H$_5$H$_3$)= 1.4), 6.81 (td, 1H, H$_3$, ^3J(H$_3$H$_4$)= 7.6,

$^4J(H_3H_5)$= 1.3), 6.55 (m, 2H, H_2/H_4), 2.36 (s, 3H, Me). ^{13}C NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 160.82 (s, C=N), 157.06 (s, C_7), 147.75 (s, C_{11}), 145.8 (s, C_1), 141.1 (s, C_9), 133.8, 127.0, 125.1, 124.2, 119.9 (s, $C_3/C_4/C_5/C_8/C_{10}$), 124.2 (s, C_6), 108.2 (s, C_2), 13.3 (s, Me). MS-FAB: m/z = 440.0 ((L-H)PtCl)$^+$. Specific molar conductivity: Λ_m = 0.31 S cm^2 mol^{-1} (in nitrobenzene).

(Pt{3-Cl-C_6H_3N(H)N=CMe(C_5H_4N)}(Cl)) (2c): Compound **2c** was obtained as an orange solid following a similar method to that used for the preparation of **1a** (**Method 1**). Yield: 35%. Anal. found: C, 32.9; H, 2.6; N, 8.6; $C_{13}H_{11}N_3Cl_2Pt$ requires C, 32.8; H, 2.3; N, 8.8. IR: ν_{max}/cm^{-1} 1589s (C=N), 3253m (N-H). ^{1}H NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 9.45 (dd, 1H, H_{11}, $^4J(H_{10}H_{11})$= 5.7, $^3J(H_9H_{11})$= 1.5), 8.84 (s, 1H, NH), 8.47 (td, 1H, H_9, $^3J(H_8H_9)$= 7.8, $^4J(H_9H_{11})$= 1.5), 8.30 (dd, 1H, H_8, $^3J(H_8H_9)$= 7.8, $^4J(H_8H_{10})$= 1.4), 7.99 (m, 1H, H_{10}), 7.65 (d, 1H, H_2, $^4J(H_2H_4)$= 2.4), 7.31 (dd, 1H, H_4, $^3J(H_4H_5)$= 8.8, $^4J(H_4H_2)$=2.4), 6.96 (d, 1H, H_5, $^3J(H_4H_5)$= 8.8), 2.34 (s, 3H, Me). MS-FAB: m/z = 475.0 ((L-H)PtCl)$^+$, 440.0 ((L-H)Pt)$^+$.

(Pt{2,4-Cl-C_6H_2N(H)N=CMe(C_5H_4N)}(Cl)) (2d): Compound **2d** was prepared following a similar procedure to that used for **2a**, as a red solid. Yield: 27%. Anal. found: C, 30.9; H, 2.0; N, 8.3; $C_{13}H_{10}N_3Cl_3Pt$ requires C, 30.6; H, 1.9; N, 8.2. IR: ν_{max}/cm^{-1} 1597s (C=N), 3292w (N-H). ^{1}H NMR (500 MHz, DMSO-d^6, δ ppm, J Hz): δ = 10.34 (s, 1H, NH, ^3J(NHPt)= 30.3), 8.59 (dd, 1H, H_{11}, $^3J(H_{10}H_{11})$= 5.2, $^4J(H_9H_{11})$= 1.7), 8.17 (dt, 1H, H_9, $^3J(H_9H_{10})$= 7.9, $^4J(H_9H_{11})$= 1.7), 7.83 (d, 1H, H_8, $^3J(H_8H_9)$= 8.0), 7.99 (m, 1H, H_{10}), 7.10 (d, 1H, H_4, $^4J(H_3H_5)$= 2.3), 6.99 (dd, 1H, H_5, $^3J(H_5$Pt)= 22.2, $^4J(H_3H_5)$= 2.3), 2.34 (s, 3H, Me). ^{13}C NMR (126 MHz, DMSO-d^6, δ ppm, J Hz): δ = 159.6 (s, C_7), 153.2 (s, C=N), 152.4 (s, C_4), 147.8 (s, C_{11}), 141.0 (s, C_9), 130.8 (s, C_5), 128.6 (s,C_1), 127.9 (s, C_{10}), 125.3 (s, C_8), 124.1 (s, C_6), 123.7 (s, C_3), 112.4 (s, C_2), 13.8 (s, Me). MS-FAB: m/z = 515.0 ((L-H)Pt(CH_3CN))$^+$.

Preparation of (Pt{2-Cl-C_6H_3N(H)N=CMe(C_5H_4N)}(Cl)) (2e): Compound **2e** was obtained as an orange solid following similar procedures to those used for the preparation of **1a: Method 1** (Yield 69%) or **Method 2 (**Yield 71%). **2e** was characterized by IR spectroscopy due to its low solubility. Yield 71%. IR: ν_{max}/cm^{-1} 1592w (C=N), 3236w (N-H).

Preparation of (Pt{(3,4-Me$_2$-C_6H_2C(Me)=NN(H)(4'-Cl-$C_4H_2N_2$)}(Cl)(PPh$_3$)) (1e): PPh$_3$ (14 mg, 0.053 mmol) was added to a suspension of **2e** (28 mg, 0.055 mmol) in acetone (10 cm^3). The mixture was stirred for 3 h and the solvent removed to give a red solid which was recrystallized from dichloromethane/ ether. Yield: 98%. Anal. found: C, 50.3; H, 3.8; N, 7.2; $C_{32}H_{29}N_4Cl_2PPt$ requires C, 50.1; H, 3.8; N, 7.3. IR: ν_{max}/cm^{-1} 1591w (C=N), 3051w (N-H). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ = 10.48 (s, 1H, NH), 8.26, 7.11 (d, 1H, H_8/H_9, $^3J(H_8H_9)$= 9.4), 6.67 (s, 1H, H_2), 5.63 (d, 1H, H_5, $^4J(H_5$Pt) = 51.6), 2.78 (s, 3H, Me(C=N)), 2.02 (s, 3H, Me(a)), 1.60 (s, 3H, Me(b)). ^{31}P NMR (300 MHz, CDCl$_3$, δ ppm, J Hz): δ = 23.61 (s, 1, PPh$_3$, ^1J(PtP)= 2075.8). MS-FAB: m/z = 730.2 ((L-H)PtPPh$_3$)$^+$. Specific molar conductivity: Λ_m = 0.95 S cm^2 mol^{-1} (in nitrobenzene).

Preparation of (Pt{(3,4-Me$_2$-C_6H_2C(Me)=NN(H)(4'-Cl-$C_4H_2N_2$)}(PPh$_3$))(F_3CSO_3) (3e): Silver trifluoromethanesulfonate (14 mg, 0.042 mmol) was added to a suspension of **1e** (21 mg, 0.042 mmol) in acetone (15 cm^3). The resulting mixture was stirred for 30 min, and then PPh$_3$ (11 mg, 0.042 mmol) was added and stirred for 5 h. The solution filtered through celite to remove the AgCl precipitate and the solvent removed to give a red solid which was recrystallized from dichloromethane/hexane. Yield: 40%. Anal. found: C, 45.1; H, 3.4; N, 6.2; $C_{33}H_{29}N_4ClPPtF_3SO_3$ requires C, 45.0; H, 3.3; N, 6.4. IR: ν_{max}/cm^{-1} 1598w (C=N), 3065w (N-H), 1056s, 1157sh, 1239m and 1288m (CF_3SO_3). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, J Hz): δ =11.84 (d, 1H, NH, ^3J(NHPt)=16.5, ^3J(NHP)= 5.4), 7.22 (d, 1H, H_8/H_9, $^3J(H_8H_9)$= 9.4), 6.67 (s, 1H, H_2), 5.67 (d, 1H, H_5, $^4J(H_5Pt)= 25.8$, $^4J(H_5P)= 1.9$), 2.55 (s, 3H, Me(C=N)), 2.03 (s, 3H, Me(a)), 1.61 (s, 3H, Me(b)). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm, *J* Hz): $\delta = 23.56$ (s, 1, PPh_3, $^1J(PtP)= 2085.4$). MS-FAB: m/z = 730.2 ($((L-H)PtClPPh_3)^+$). Specific molar conductivity: $\Lambda_m = 107$ S cm^2 mol^{-1} (in acetonitrile).

(Pt{(3,4-Me$_2$-C$_6$H$_2$C(Me)=NN(H)(4'-Cl-C$_4$H$_2$N$_2$)}(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-P,P,P)(Cl) (4e): Compound **4e** was obtained following a similar procedure that the compound **2e** as a green solid. Yield: 58%. Anal. found: C, 55.6; H, 4.5; N, 5.2; $C_{48}H_{47}N_4Cl_2P_3Pt$ requires C, 55.5; H, 4.6; N, 5.4. IR: ν_{max}/cm^{-1} 1591w (C=N), 3050w (N-H). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, *J* Hz): $\delta = 10.62$ (s, 1H, NH), 6.73 (d, 1H, H_8/H_9, $^3J(H_8H_9)= 9.2$), 6.50 (sa, 1H, H_2), 5.55 (d, 1H, H_5, $^3J(H_5Pt)= 16.3$, $^4J(H_5P_{central})= 6.3$), 2.26 (s, 3H, Me(C=N)), 2.03 (s, 3H, Me(a)), 1.40 (s, 3H, Me(b)). ^{31}P NMR (300 MHz, $CDCl_3$, δ ppm, *J* Hz): $\delta = 86.66$ (s, 1P, $P_{central}$, $^1J(PtP)= 859.2$), 37.12 (s, 2P, $P_{terminal}$, $^1J(PtP) = 1631.1$). MS-FAB: m/z = 1002.0 ($((L-H)Pt(trifos))^+$). Specific molar conductivity: $\Lambda_m = 106$ S cm^2 mol^{-1} (in acetonitrile).

({Pt(3,4-(Me)$_2$C$_6$H$_2$C(Me)=NN(H)(4'ClC$_4$H$_2$N$_2$))}$_3${μ$_3$-(PPh$_2$CH$_2$CH$_2$)$_2$PPh})(Cl)$_3$, (5e). $PPh_2CH_2CH_2)_2PPh$ (17.6 mg, 0.033 mmol) was added to a suspension of **1e** (50 mg, 0.099 mmol) in acetone (15 cm^3). The resulting mixture was stirred at room temperature for 48 h and the resulting solution and the yellow-green solid formed was filtered off and dried in air. Yield: 31.1 mg (54%). Anal. found: C, 42.1; H, 3.5; N, 8.0; $C_{73}H_{69}Cl_6N_{12}Pt_3P_3$ requires C, 43.7; H, 3.5; N, 8.4. IR: ν_{max}/cm^{-1} 1595m (C=N), 3275m (N-H). ^{1}H NMR (300 MHz, DMSO-d^6, δ ppm, *J* Hz): $\delta = 5.49$ (s, 1H, H_5), 5.06 (s, 2H, H_5), 2.79 (s, 6H, Me(C=N)), 2.75 (s, 3H, Me(C=N)), 2.02 (s, 6H, Me), 1.94 (s, 3H, Me), 1.53 (s, 6H, Me), 1.21 (s, 3H, Me). ^{31}P NMR (121.49 MHz, dmso-d^6, δ ppm): $\delta = 28.0$ (s, $^1J(PtP)= 4125$), 24.1 (s, $^1J(PtP)= 4098$).

3. Computational Methods

All quantum chemical calculations were carried out with the Gaussian 09 suit of programs. [8] Geometry optimizations of the molecular structures of reactives, intermediates, products and transition states have been performed with the M06 method, which employs the hybrid meta exchange-correlation functional of Truhlar and Zao, [9] using basis set I (BS1), and the default integration grid. [10] With BS1, the inner electrons of Pt are described by the Stuttgart/Cologne fully relativistic effective-core potential (ECP60MDF, replacing 60 core electrons) and the associated double-zeta basis set (ECP60MDF_VDZ) is used for the outer electrons. [11,12] All other atoms (C, H, Cl, N and O) are described with the Dunning´s correlated consistent double-ζ basis sets [13] (cc-pVDZ, as implemented in Gaussian 09). [14,15] Molecular structures were fully optimized without constraints, with optional consideration of one explicit solvent (*n*-BuOH) molecule, in the solvent phase ((SCRF)M06/BS1 level). For the solvent phase calculations, the polarizable continuum solvation model with the integral equation formalism variant (IEF-PCM) [16] was used as implemented in Gaussian 09. The IEF-PCM parameters were selected

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10 The default integration grid in Gaussian 09 (Fine grid, using SSF atomic partitioning function, Euler-Maclaurin radial quadrature, 75 radial shells and 302 angular points per shell) is a pruned grid that has considerably better numerical accuracy and rotational invariance than SG1 (50 radial shells and 194 angular points per shell) grid which, in turn, was not recommended for production calculations with meta-GGA functionals, see: S. E. Wheeler, K. N. Houk, *J. Chem. Theory Comput.*, 2010, **6**, 395-404.

11 D. Figgen, K. A. Peterson, M. Dolg, H. Stoll, *J. Chem. Phys.*, 2009, **130**, 164108.

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14 Truhlar's group have demonstrated improved performance of the M06 functionals as compared to the more widely used B3LYP method for studying reactions involving transition metals, see: Y. Zhao, D. G. Truhlar, *Chem. Phys. Lett.*, 2011, **502**, 1-13.

15 Geometric parameters obtained by gas-phase optimization at B3LYP/BS1 or M06/BS1 level for a representative set of X-ray diffraction structures of cycloplatinated compounds were found to be very similar (see Supplementary Information, Table S1). In addition, Pt-N, Pt-C and Pt-Cl bond distances calculated M06/BS1 level were found in better agreement with the X-ray diffraction values than those numbers obtained by using M06 functional in combination with other polarized double–ζ basis sets and effective core potentials.

for pure *n*-butanol as solvent (dielectric constant of 17.332) and atomic radii from universal force field were used for the solute atomic radii. Vibrational frequencies were calculated analytically at the same level to ensure that each minimum is a true local minimum (only positive frequencies) and that each transition structure has only a single imaginary frequency (negative eigenvalue in the Hessian matrix). These calculations were also used to determine the difference between the free and electronic energies (G–E), which include zero-point vibrational energy, thermal and entropy corrections at the reaction conditions (1 atm and 315.15 K). Intrinsic reaction coordinates (IRC) [17] were employed to verify the connection of relevant transition structures to the respective minima.

Single-point energies were calculated on the solvent-phase optimized structures using the M06 method with the Grimme´s dispersion correction [18] (D3 damping function), an extended basis set (BS2) and the polarizable continuum solvation model (IEF-PCM). With BS2, C, H, Cl, N and O atoms are described with the Dunning´s minimally augmented triple-ζ basis sets (maug-cc-pV(T+d)Z) [19,20,21] and Pt is described with ECP60MDF along with the corresponding fully augmented triple-ζ basis set (ECP60MDF_AVTZ).[11,12] Natural population, natural bond orbital (NBO) and second-order perturbation theory analyses were performed on solvent-phase optimized structures at the same level ((SCRF)M06+D3/BS2//(SCRF)M06/BS1), with the NBO software (version 3.1) [22] as implemented in Gaussian 09. All of the energies given in text are free energies of solutes in the condensed phase, which were calculated by adding the thermodynamic corrections (G–E) to the "botton-of-the-well" electronic energies calculated in solution. The energies of intermediates and transition states along with the byproducts are indicated relative to the starting compounds (ligands **a**-**d**) and reagents ($(PtCl_4)^{2-}$ and acetate or *n*-BuOH for some pathways).

To evaluate the energy of stacking interactions, dimers formed by two stacked molecules were obtained from the crystal structures of **2e-dmso** and CDS ref-code IGIHIQ and single point calculations were performed using the hybrid functional of Tao, Perdew, Staroverov and Scuseria (TPSS) [23] with the Grimme´s dispersion correction [18] (D3 damping function) and the new formulations of the triple-ζ basis set of Alrich (def2-TZVP) [24] For this calculations, the basis set superimposition error was removed by the counterpoise correction [25], as implemented in Gaussian 09.

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17 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363-68.

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20 For density functional calculations, Dunning´s minimally augmented basis sets (maug-cc-pv(X+d)Z) have proven to be as accurate as the fully augmented ones (aug-cc-pv(X+d)Z) but producing computational cost savings of about a factor of two to seven, see: E. Papajak, D. G. Truhlar, *J. Chem. Theory Comput.*, 2010, **6**, 597-601.

21 Dunning´s minimally augmented basis sets and DZP-DKH basis sets were downloaded from the Basis Set Exchange (BSE) web, see: (a) K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045-1052; (b) D. Feller, *J. Comp. Chem.*, 1996, **17**, 1571-1586.

22 (a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO version 3.1; (b) A. E. Reed, R. B. Weinstock, F. J. Weinhold, *Chem. Phys.*, 1985, **83**, 735-746.

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Computed structures were illustrated using CYLview. [26]

NCI computations have been carried out with the NCIPLOT software version 3.0.[27] NCI isosurfaces were obtained from SCF and/or promolecular densities calculated on selected solvent-phase optimized geometries (at (SCRF)M06/BS1 level) and for the monomer and dimer in the crystal structure of **2e-dmso**. SCF densities were calculated using the M06 method in conjuction with the Douglas-Kroll-Hess second order scalar relativistic calculation [28] and all electron contracted double-ζ plus polarization basis set (DZP-DKH). [29] Promolecular densities were constructed from the atomic positions stored in the xyz coordinate files as implemented in NCIPLOT. The NCI regions were visualized with Visual Molecular Dynamics software version 1.9.3. [30]

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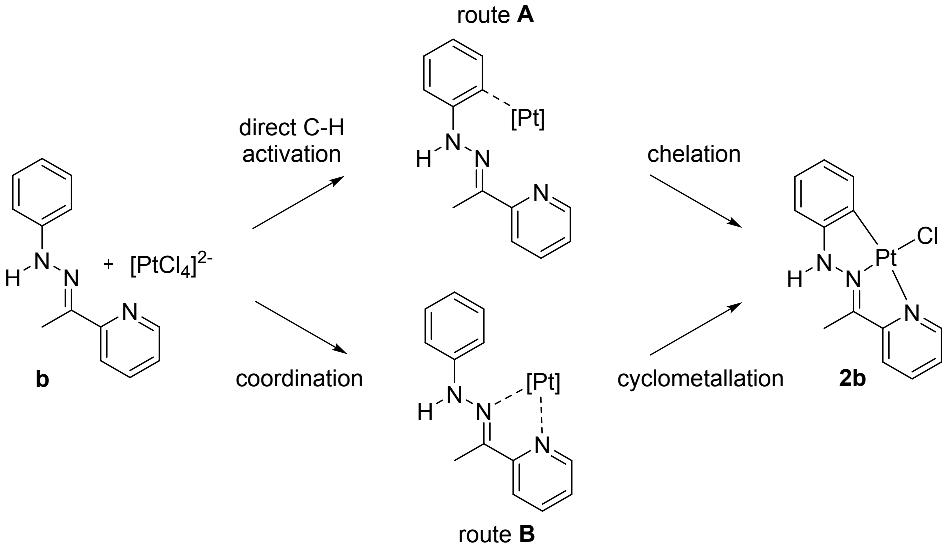
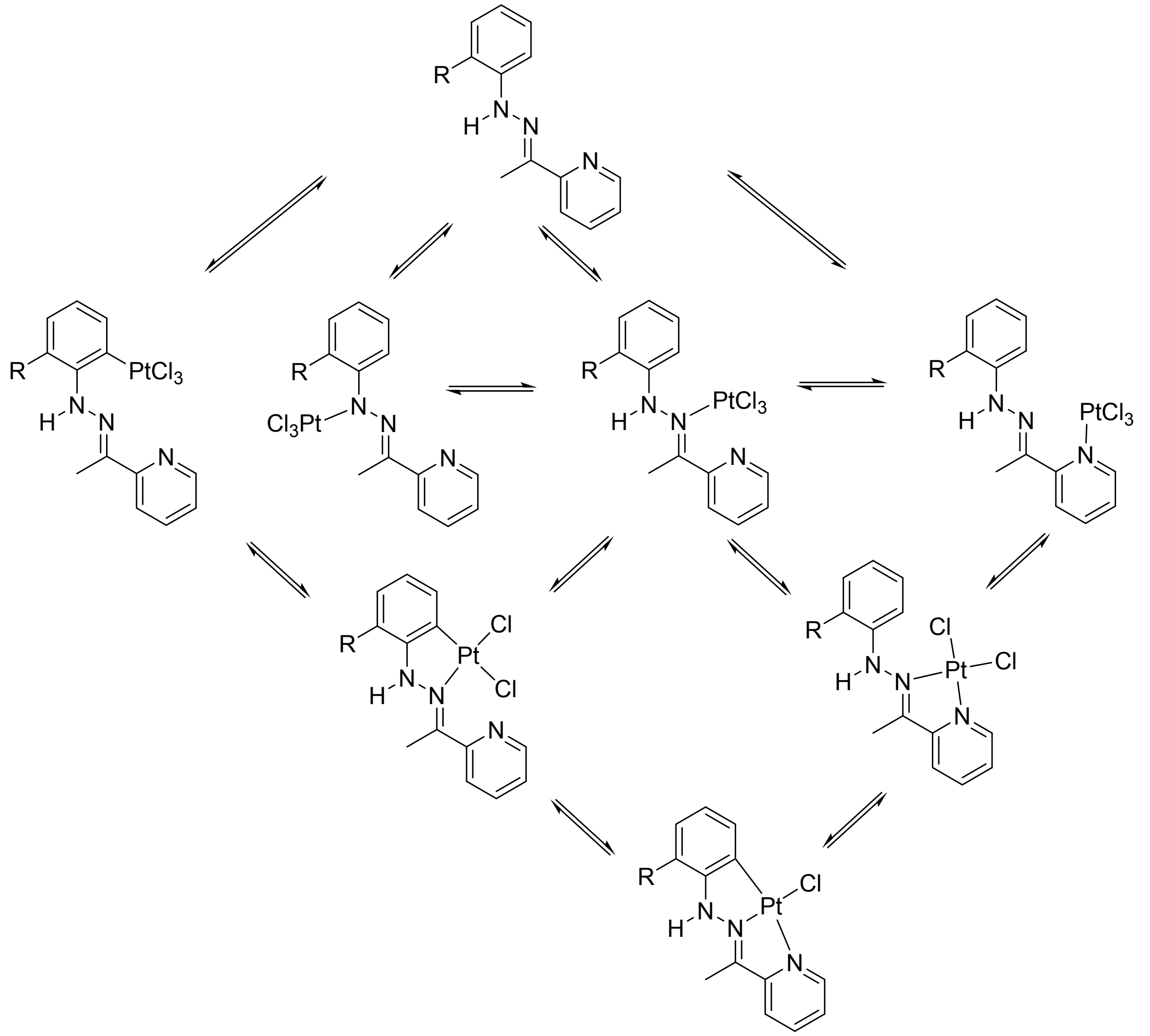
5. Additional DFT computational results.

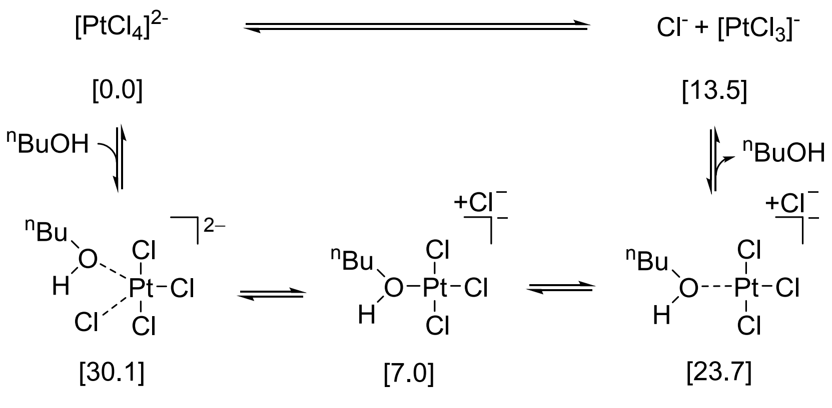
Scheme S3A. Major reaction routes to cycloplatinated complex **2b.**



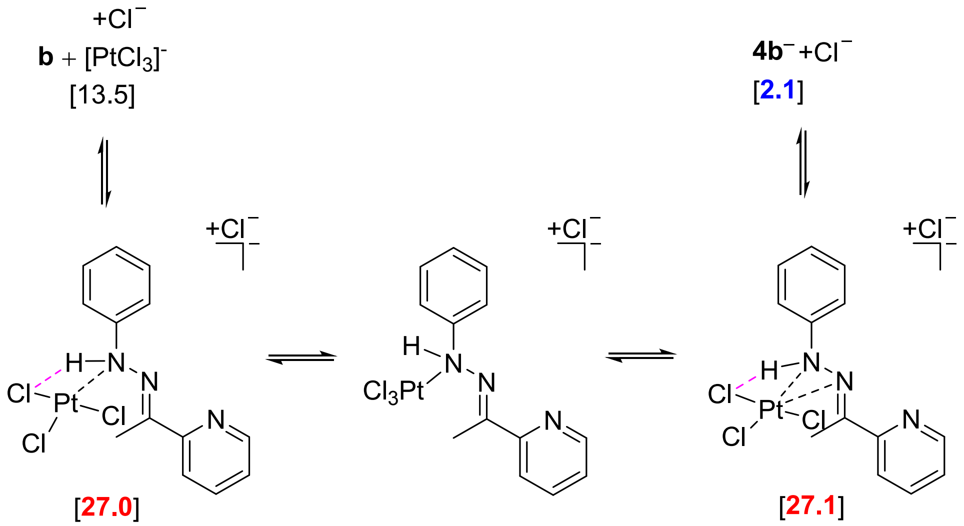
Scheme S3B. Mechanistic posibilities to cycloplatinated complexes **2a,b** that have been computed



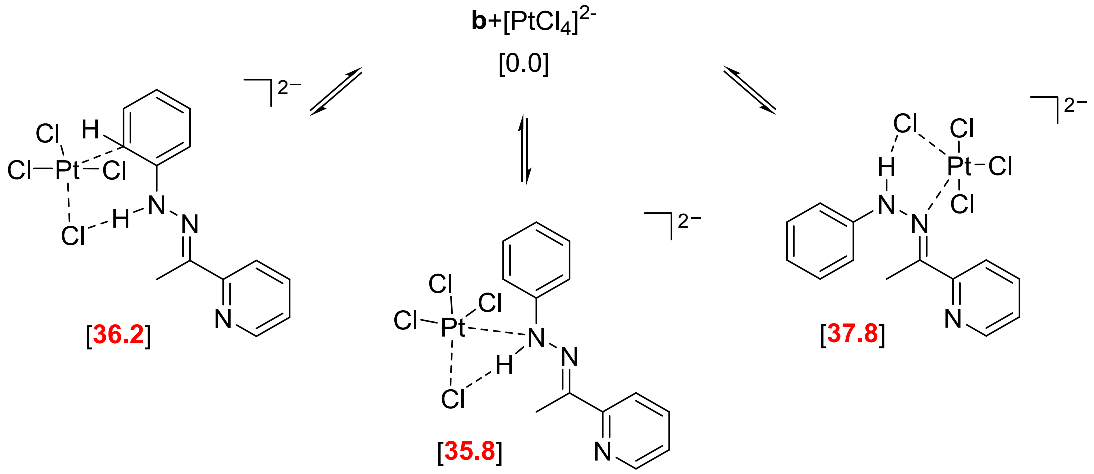
Scheme S4. Dissociation of $[PtCl_4]^{2-}$ in butanol solution. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



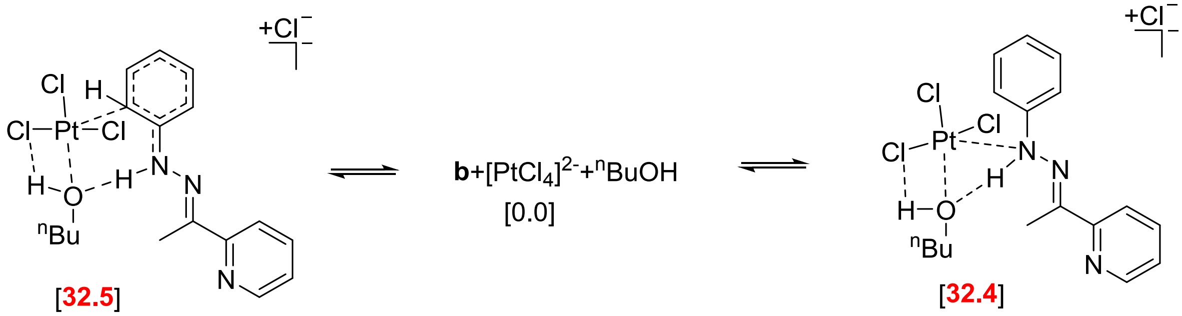
Scheme S5. Competitive pathways for dissociative substitution on $[PtCl_4]^{2-}$ with the amino and the imino groups of ligand **b** acting as nucleophiles. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



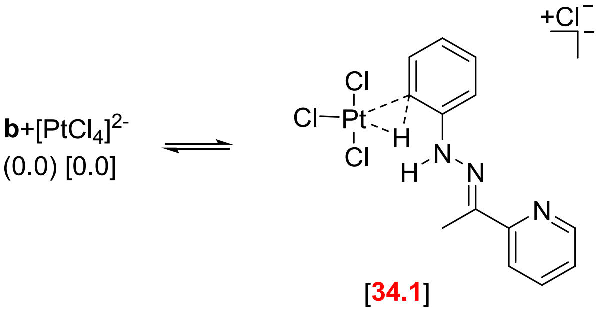
Scheme S6. Competitive transition structures for the concerted (interchange) substitution on $[PtCl_4]^{2-}$ with the phenyl, amino, or imino groups of ligand **b** acting as nucleophiles. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



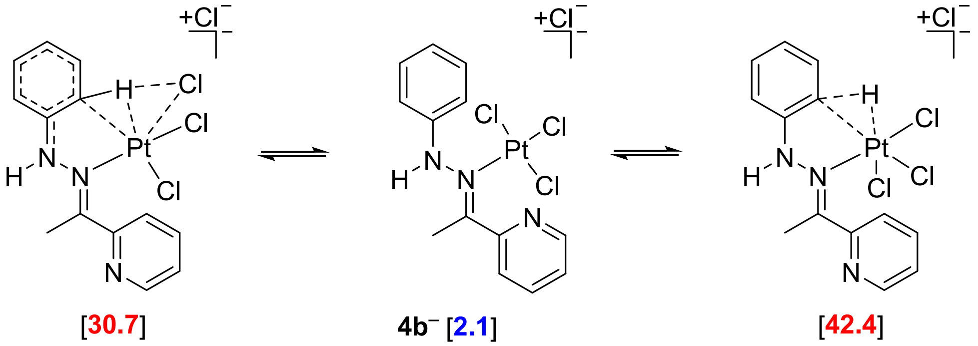
Scheme S7. Solvent assisted pathways for chloride substitution on $[PtCl_4]^{2-}$ with the amino or the phenyl groups of ligand **b** acting as nucleophiles. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



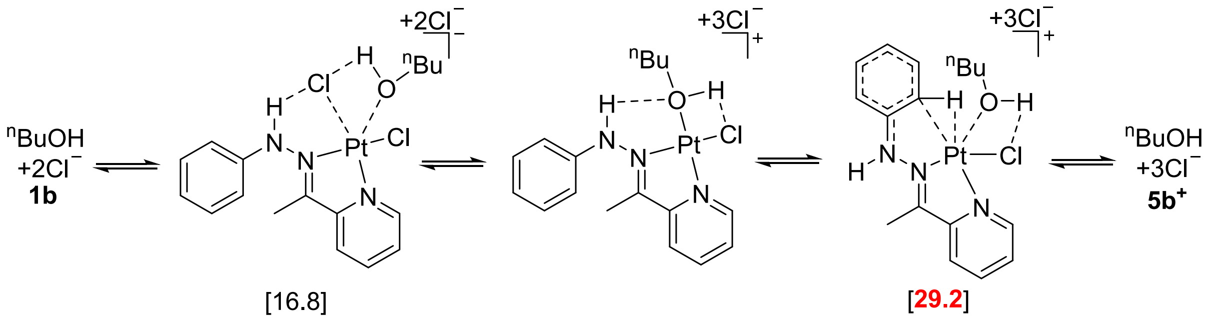
Scheme S8. Transition structure for direct activation of C-H bond in ligand **b** by $[PtCl_4]^{2-}$. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



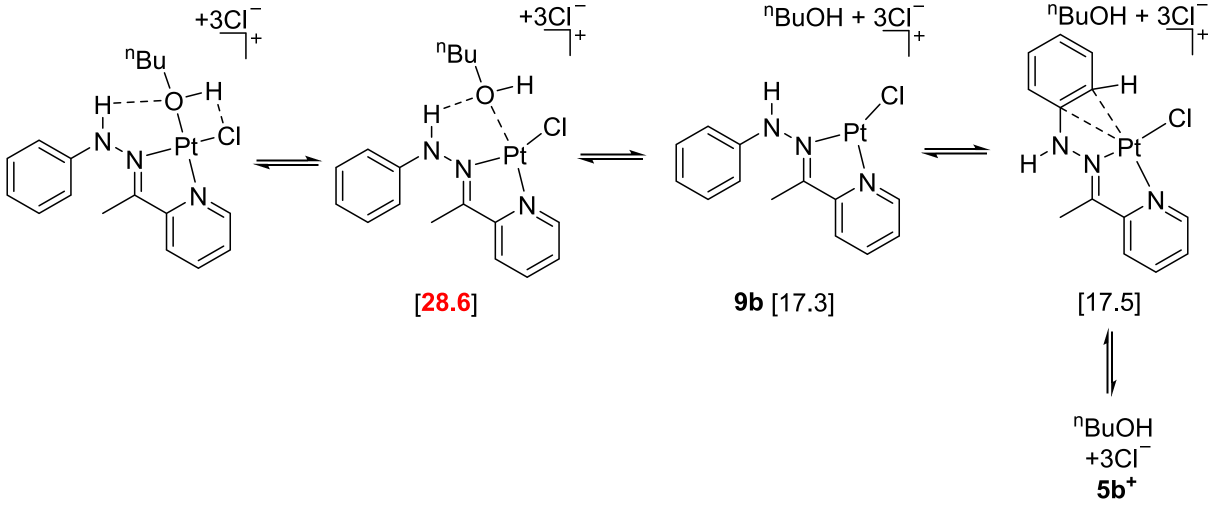
Scheme S9. Transition structures located for the cyclometallation of intermediate **4b⁻** by electrophilic substitution or oxidative addition pathways. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



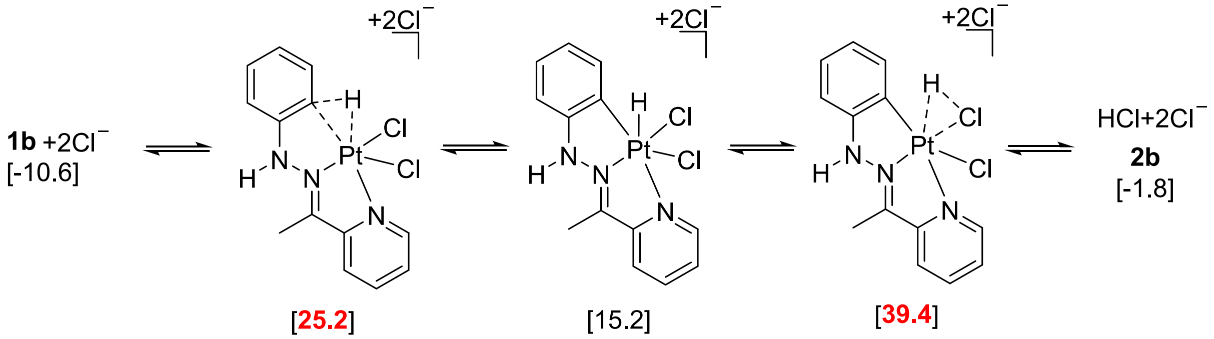
Scheme S10. Prequilibrium of chelate intermediate **1b** with solvent complexes followed by direct electrophilic substitution. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



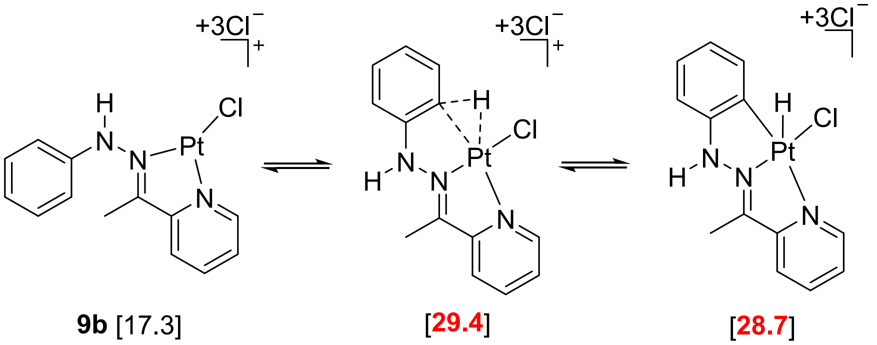
Scheme S11. Prequilibrium of chelate intermediate **1b** with solvent complexes followed by dissociative electrophilic substitution. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



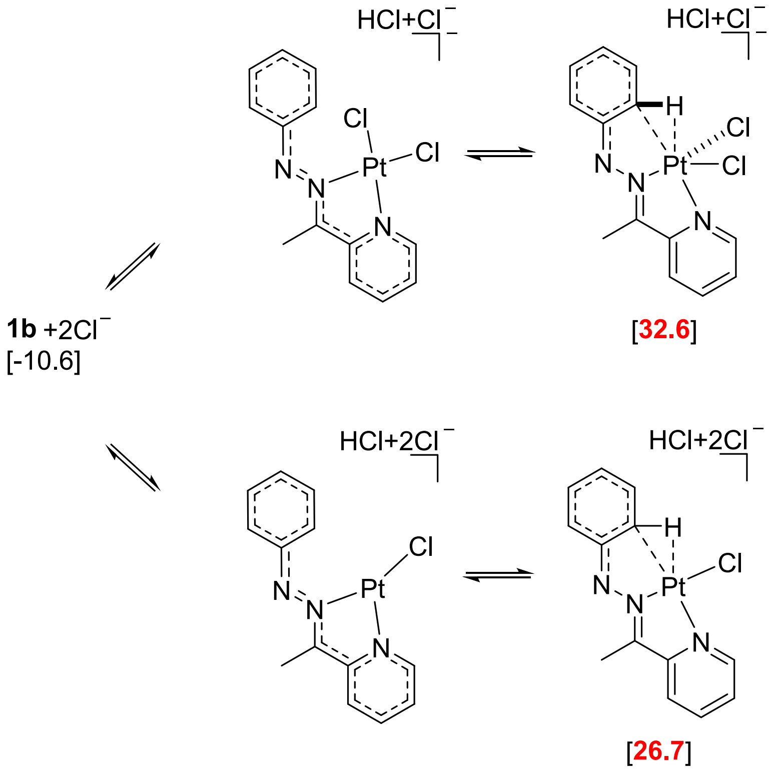
Scheme S12A. Cyclometallation of intermediate **1b** by oxidative addition routes. Free energies in butanol solution at 373 K (kcal/mol) calculated on solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



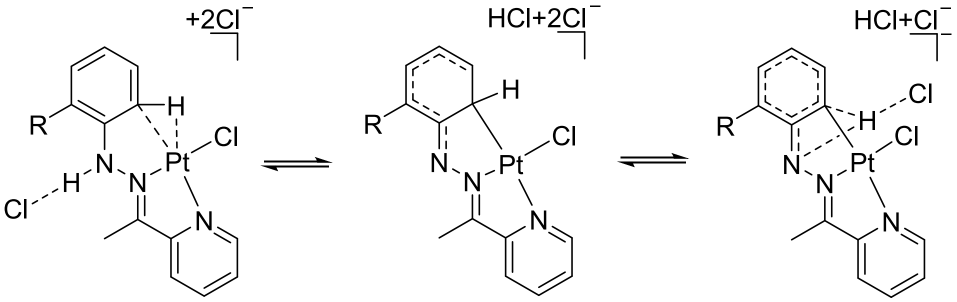
Scheme S12B. Cyclometallation of intermediate **1b** by oxidative addition routes. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



Scheme S13. Deprotonation of chelate intermediate **2b** followed by electrophilic substitution. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



Scheme S14. Deprotonation of intermediate **5b^{HB}** followed by aromatization**.** Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].

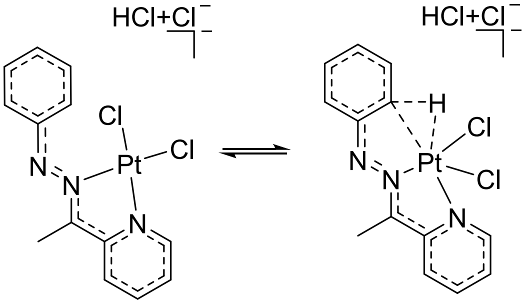


5a^{HB} [14.0]
5b^{HB} [9.3]

6a [16.0]
6b [15.7]

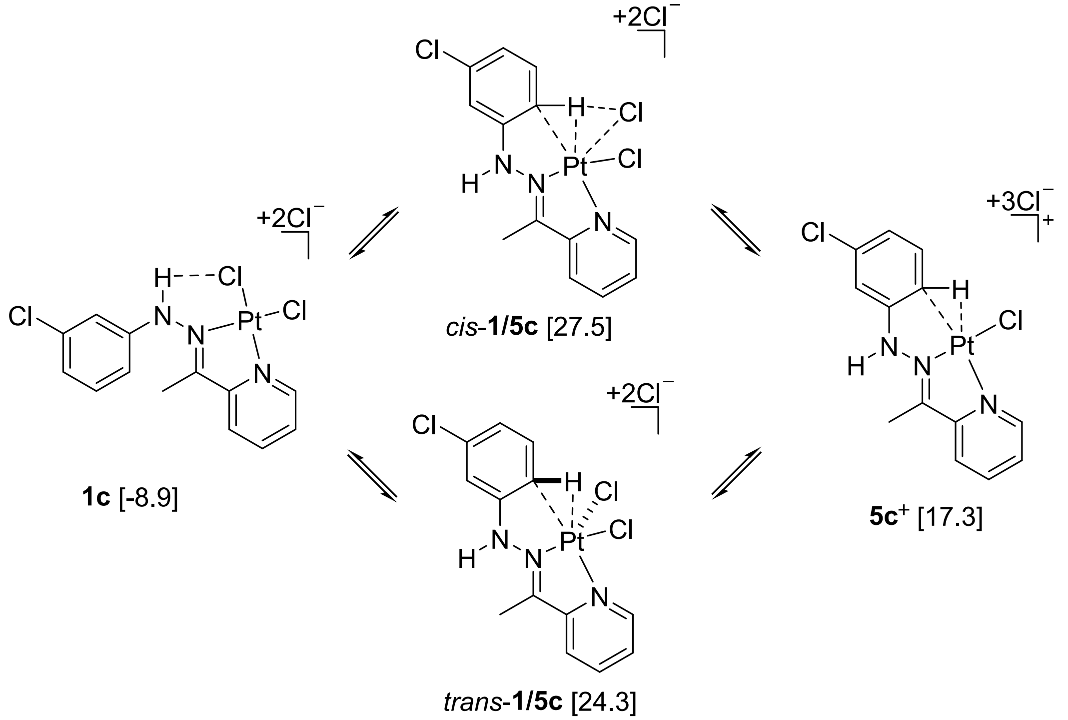
6/1a [**24.0**]
6/1b [**25.1**]

Scheme S15. Deprotonation of chelate intermediate **2b** followed by oxidative addition route**.** Free energy in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized transition structure is included in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].

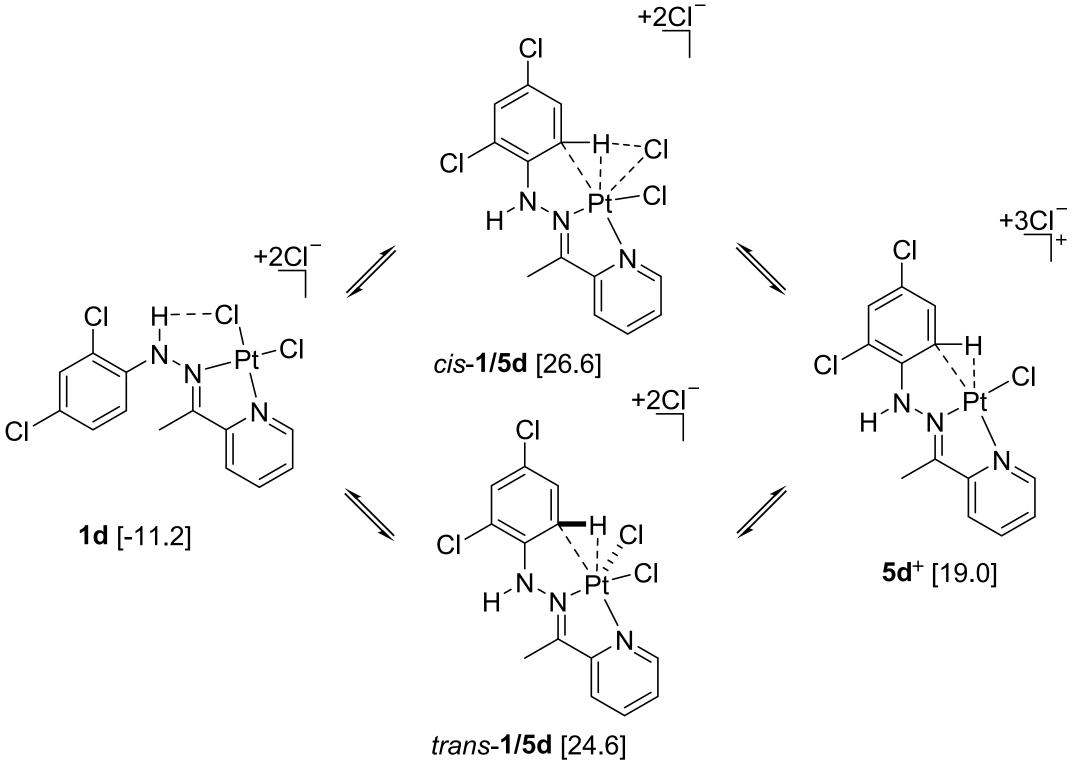


[**36.1**]

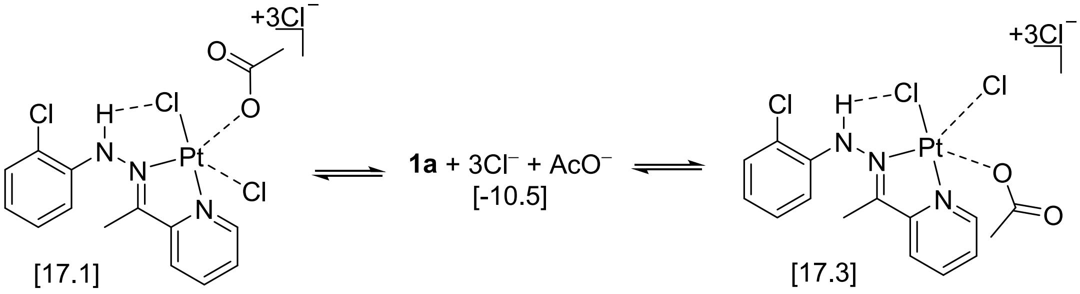
Scheme S16A. Direct electrophilic substitution on 3-chloro substituted chelate intermediate **1c.** Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



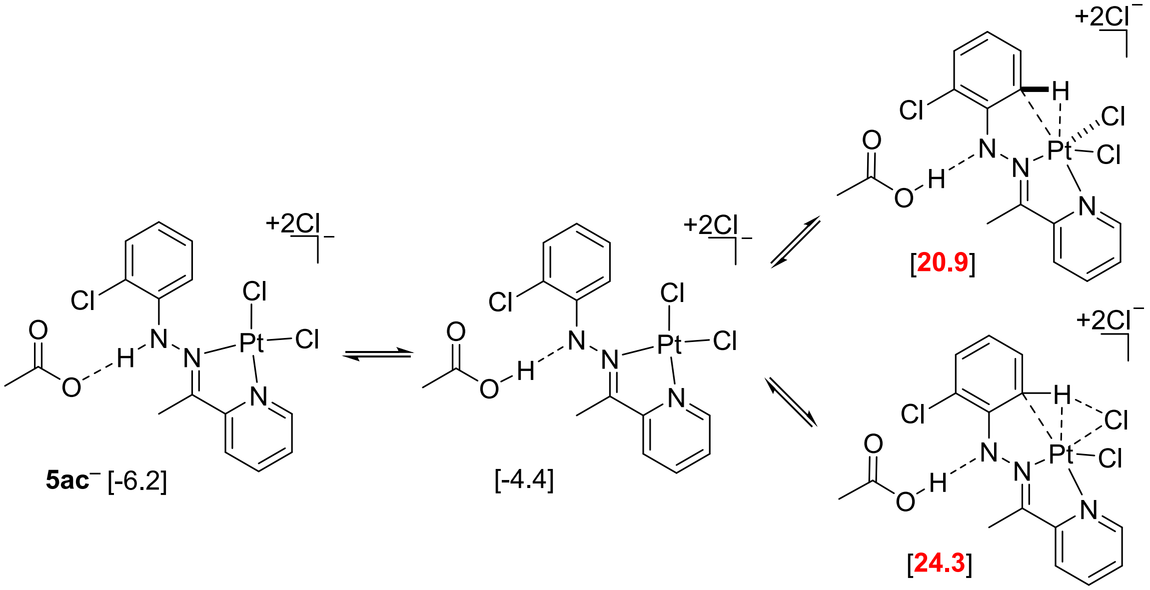
Scheme S16B. Direct electrophilic substitution on 2,4-dichloro substituted chelate intermediate **1d.** Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



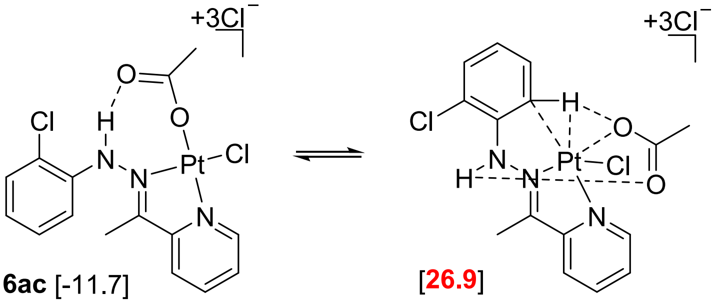
Scheme S17. Direct nucleophilic substitution of chloride by acetate anion on chelate **1a.** Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



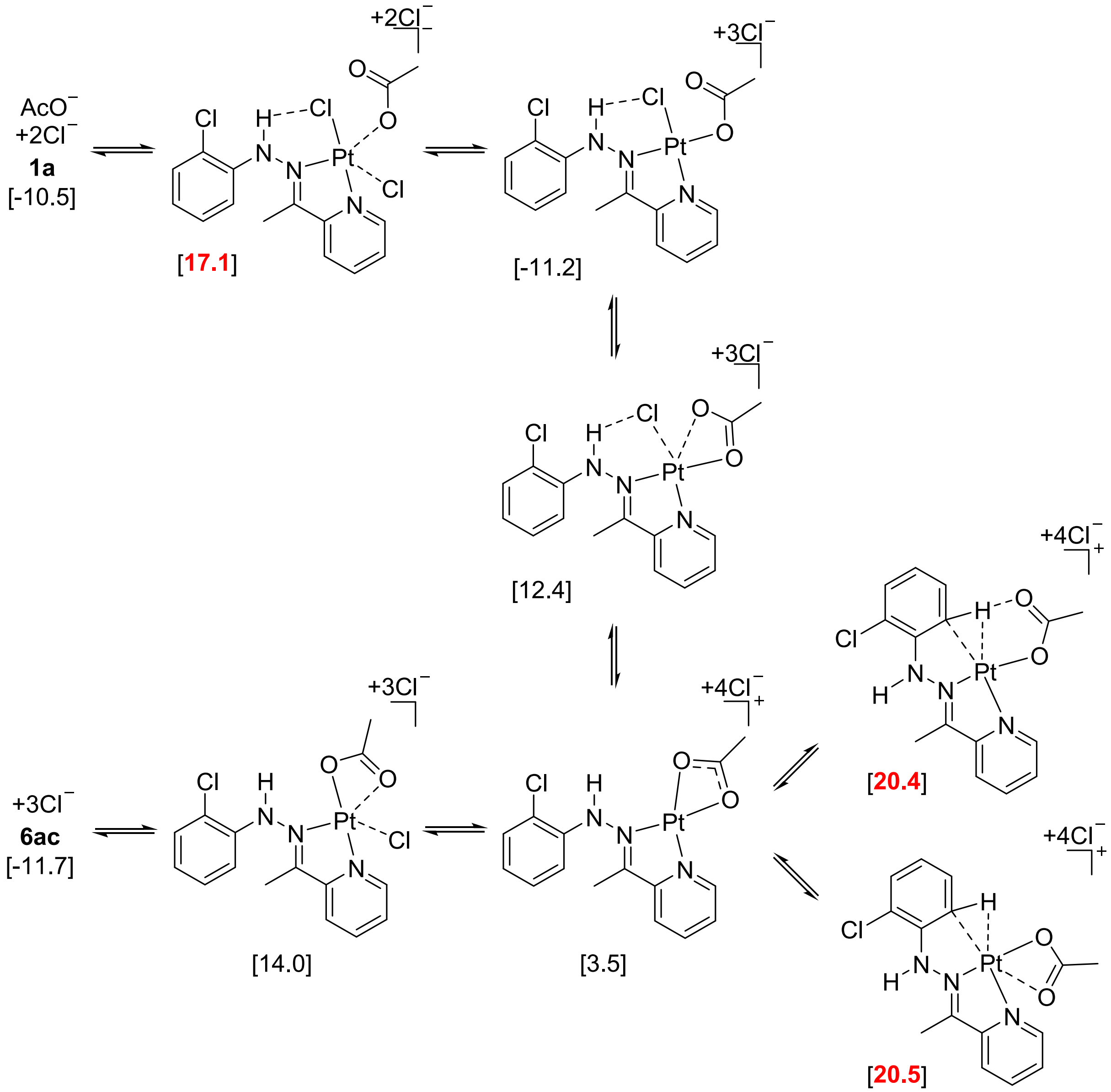
Scheme S18A. Alternative routes for cyclometallation in the presence of acetate anion by direct nucleophilic substitution of chloride ligand on the Pt(II) center. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].



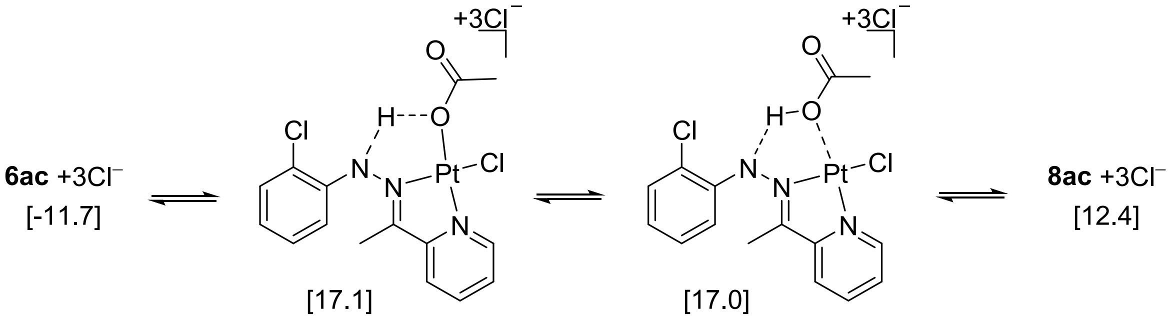
Scheme S18B. Alternative route for cyclometallation in the presence of acetate anion by direct nucleophilic substitution of acetate ligand on the Pt(II) center. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].

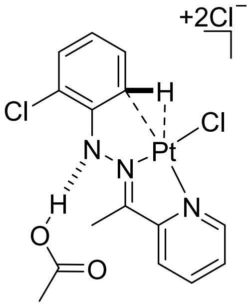


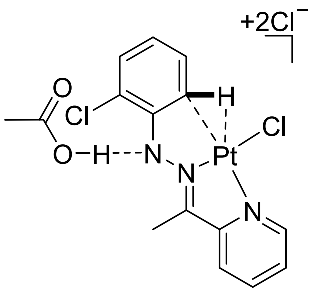
Scheme 19 Alternative cyclometallation routes through acetate bound Pt(II) complex showing K^2-coordination. Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].

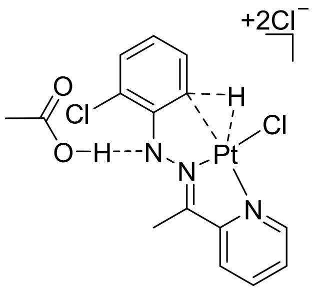


Scheme S20. Alternative transition structures for cyclometallation in the presence of acetate anion by the electrophilic substitution or oxidative addition (dissociative pathways). Free energies in butanol solution at 373 K (kcal/mol) calculated on the solution-phase optimized geometries are shown in brackets [(SCRF)M06+D3/BS2//(SCRF)M06/BS1 level].









trans-**8/9ac** [14.2]

8/9ac [12.8]

[19.7]

Figure S1. NCI-plot derived 2D representations of reduced density gradient (*s*, in au) versus electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ_2)ρ, in au), evaluated on cuboid grids, with a 0.1 au step size for the SCF density of *trans*-**1/5b.** (a) Density cut-off of 0.7 au, color scale in the -0.07 < sign(λ_2)ρ < 0.05 au range. (b) Density cut-off of 0.008 au, color scale in the -0.011 < sign(λ_2)ρ < 0.011 au range.

(a) (b)

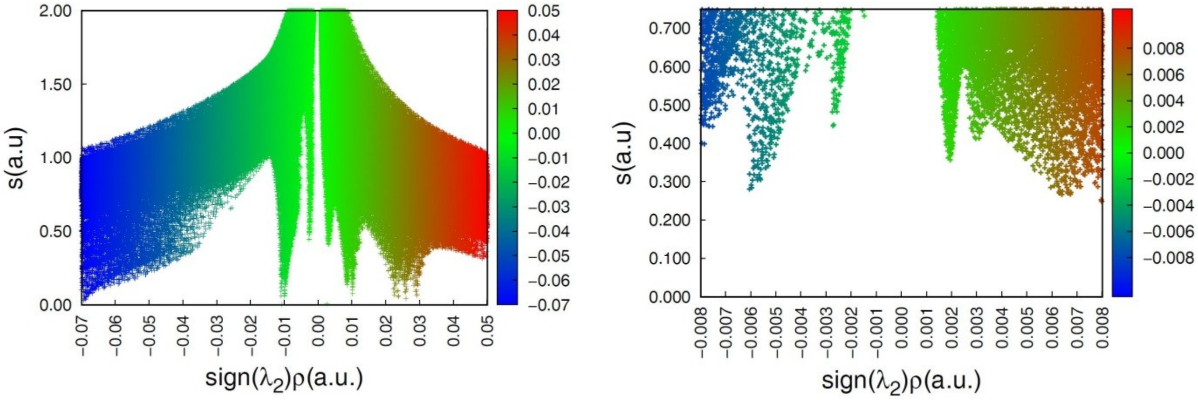


Figure S2A. Promolecular gradient isosurfaces calculated for transition structure *trans*-**1/5b**, colored on a BGR scale: blue for attractive interaction, green for weak interaction and red for steric clashes. Region of strong stabilizing agostic interaction highlighted in cyan, region of weakly non-bonding interactions between leaving chloride and *N*-phenylhydrazone moiety highlighted in green. (a) NCI isosurface with $s^{pro} = 0.30$, color scale in the $-0.07 < \text{sign}(\lambda_2)\rho^{pro} < 0.05$ au range. (b) NCI isosurface with $s^{pro} = 0.5$ with a density cut-off of $\rho^{pro} = 0.01$, color scale in the shorter $-0.015 < \text{sign}(\lambda_2)\rho^{pro} < 0.015$ au range.

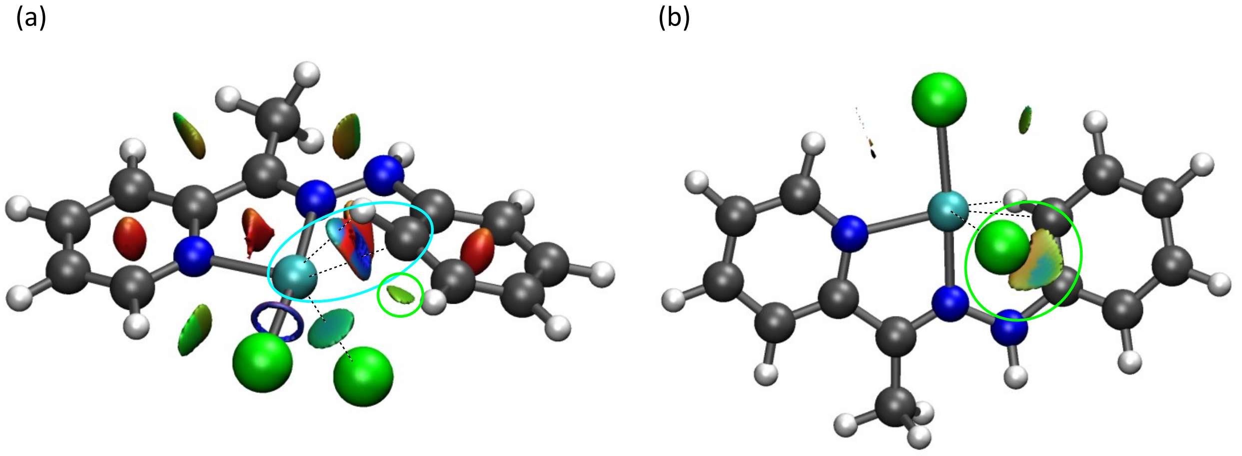


Figure S2B. NCI-plot derived 2D representations of reduced density gradient (s^{pro}, in au) versus electron density multiplied by the sign of the second Hessian eigenvalue ($\text{sign}(\lambda_2)\rho^{pro}$, in au), evaluated on cuboid grids, with a 0.1 au step size for the promolecular desity of *trans*-**1/5b.** (a) Density cut-off of 0.2 au, color scale in the $-0.07 < \text{sign}(\lambda_2)\rho^{pro} < 0.05$ au range. (b) Density cut-off of 0.01 au, color scale in the shorter $-0.015 < \text{sign}(\lambda_2)\rho^{pro} < 0.015$ au rang.

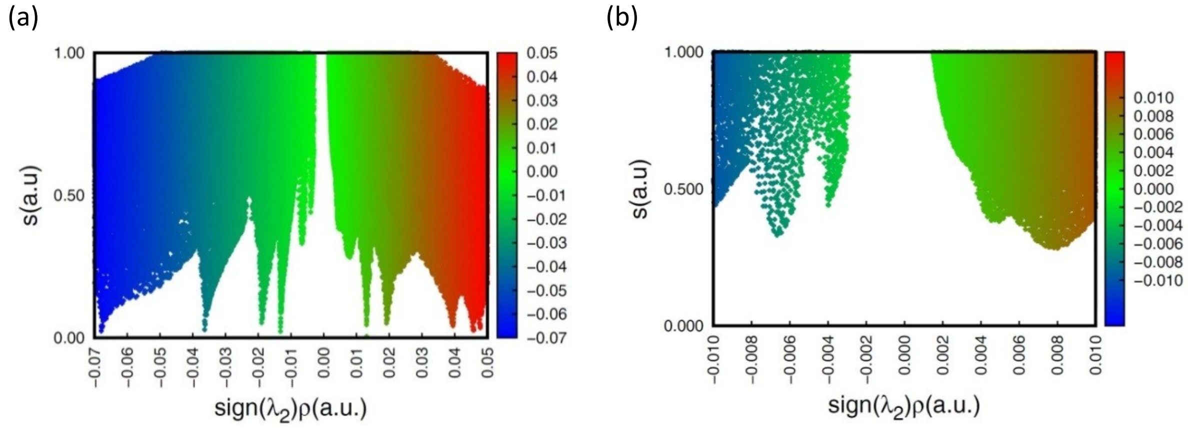


Figure S3A. NCI analysis of transition structure **8ac**. Gradient isosurfaces are colored on a BGR scale, according to the values of sign(λ_2)ρ: blue for attractive interaction, green for weak interaction and red for repulsive steric clashes. Regions of weakly non-bonding interactions between the Pt(II)center and the acetic acid moiety and the chloride substituent of the phenyl ring highlighted in green. (a) NCI isosurface with *s* = 0.4, color scale in the -0.07 < sign(λ_2)ρ < 0.05 au range. (b) NCI isosurface with *s* = 0.5 with a density cut-off of ρ = 0.010, color scale in the shorter -0.015 < sign(λ_2)ρ < 0.015 au range, to highlight the differences between attractive and repulsive dispersion interactions.

(a) (b)

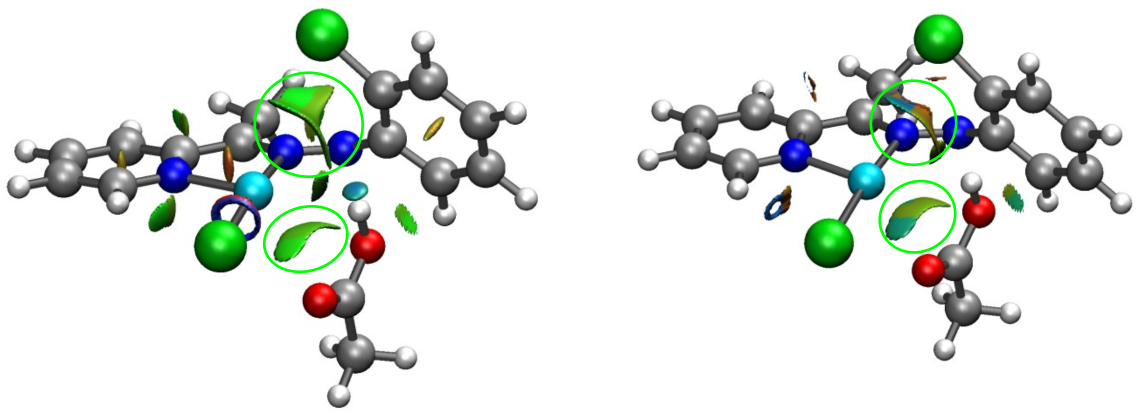


Figure S3B. NCI-plot derived 2D representations of reduced density gradient (*s*, in au) versus electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ_2)ρ, in au), evaluated on cuboid grids, with a 0.1 au step size for the SCF density of **8ac.** (a) Density cut-off of 0.7 au, color scale in the -0.07 < sign(λ_2)ρ < 0.05 au range. (b) Density cut-off of 0.010 au, color scale in the -0.015 < sign(λ_2)ρ < 0.015 au range.

(a) (b)

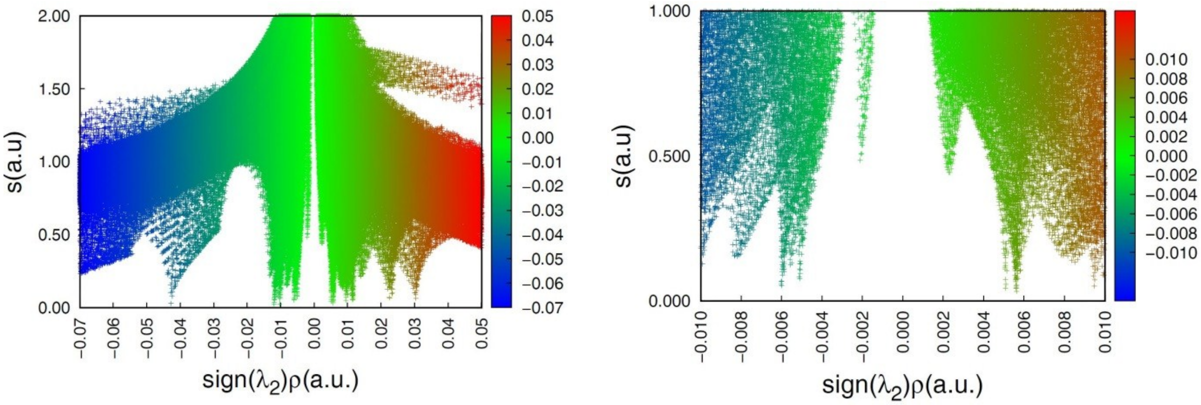


Figure S4. NCI-plot derived 2D representations of reduced density gradient (*s*, in au) versus electron density multiplied by the sign of the second Hessian eigenvalue (sign(λ_2)ρ, in au) for the promolecular density of **1e-dmso**, evaluated on cuboid grids, with a 0.1 au step size (a) Monomer, density cut-off of 0.7 au, color scale in the -0.07 < sign(λ_2)ρ < 0.05 au range. (b) Dimeric unit, density cut-off of 0.7 au, color scale in the -0.03 < sign(λ_2)ρ < 0.03 au range. (c) Dimeric unit, density cut-off of 0.010 au, color scale in the -0.01 < sign(λ_2)ρ < 0.01 au range.

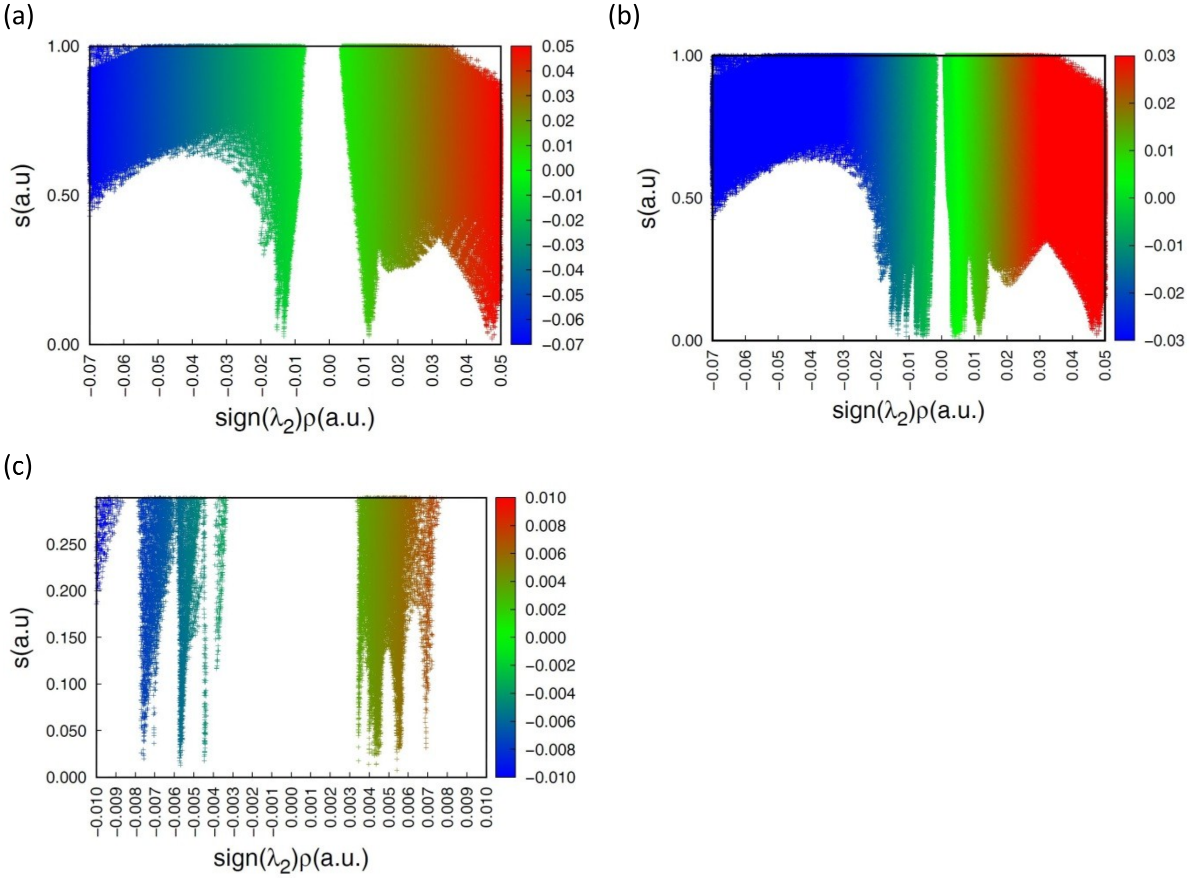


Table S1. Calculated distances obtained by gas-phase optimization of X-ray diffraction structures for a set of cycloplatinated compounds using different hybrid functional, polarized double-ζ basis set and ECP [Pt] combinations. (BS1 = cc-pVDZ[H,C,Cl,N,O],ECP60MDF_VDZ[Pt]; BS3 = cc-pVDZ[H,C,Cl,N,O],LANL2DZ[Pt]; BS4 = 6-31G(d,p)[H,C,Cl,N,O],LANL2DZ[Pt]; BS5 = Def2SVP, BS6 = 6-31G(d,p)[H,C,Cl,N,O],ECP60MDF_VDZ[Pt])

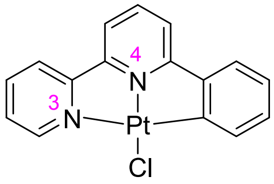
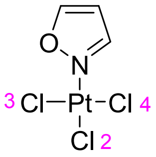
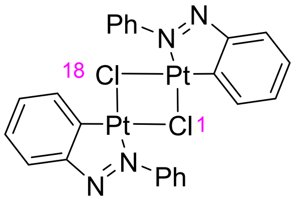
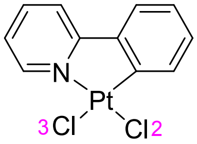
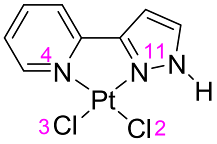
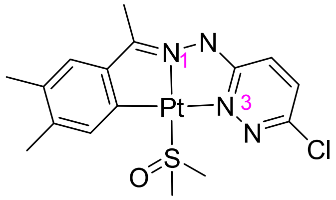
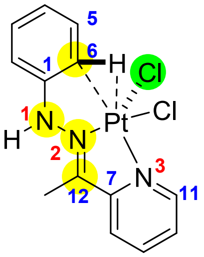
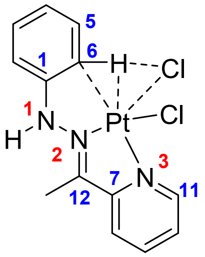
CSD ref-code **NNCRED**	**Distance (Å)**	**Pt-N3**	**Pt-N4**	**Pt-C**	**Pt-Cl**
	X-Ray	2.1244224	1.9462360	2.0142042	2.3154730
	B3LYP/BS1	2.1564615	1.9698439	1.9932715	2.3259077
	M06/BS1	2.1667445	1.9737142	1.9883980	2.3228541
	M06/BS3	2.2001680	1.9873589	1.9887168	2.3442143
	M06/BS4	2.1905400	1.9856103	1.9919494	2.3494715
	M06/BS5	2.1859861	1.9840485	1.9906784	2.3289353
	M06/BS6	2.1672295	1.9755394	1.9892700	2.3258137
CSD ref-code **JIQRUW**	**Distance (Å)**	**Pt-N**	**Pt-Cl2**	**PtCl3**	**PtCl4**
	X-Ray	1.9188731	2.3547868	2.2756261	2.3206141
	B3LYP/BS1	2.0114681	2.3175494	2.3601719	2.3859378
	M06/BS1	2.0272128	2.3132145	2.3528037	2.3789256
	M06/BS3	2.0547272	2.3310918	2.3749611	2.4068922
	M06/BS4	2.0488395	2.3359071	2.3781619	2.4073552
	M06/BS5	2.0510410	2.3165749	2.3560869	2.3977548
	M06/BS6	2.0269150	2.3136533	2.3535435	2.3793283
CSD ref-code **PAZPCP**	**Distance (Å)**	**Pt-N**	**Pt-C**	**Pt-Cl1**	**Pt-Cl18**
	X-Ray	1.9763064	1.9439222	2.3259484	2.4596118
	B3LYP/BS1	2.0279415	1.9733916	2.3744931	2.5359164
	M06/BS1	2.0316079	1.9688187	2.3709582	2.5359342
	M06/BS3	2.0416551	1.9717191	2.3953577	2.5705272
	M06/BS4	2.0378621	1.9745830	2.3973897	2.5648750
	M06/BS5	2.0436423	1.9694619	2.3845238	2.5589075
	M06/BS6	2.0319839	1.9687845	2.3720994	2.5387514
CSD ref-code **ZUDGAG**	**Distance (Å)**	**Pt-N**	**Pt-C**	**Pt-Cl2**	**Pt-Cl3**
	X-Ray	2.0145711	1.9924938	2.3294949	2.3943531
	B3LYP/BS1	2.0426928	1.9878127	2.3398330	2.4610206
	M06/BS1	2.0519655	1.9858909	2.3345126	2.4493039
	M06/BS3	2.0660190	1.9903999	2.3556117	2.4898840
	M06/BS4	2.0635567	1.9926664	2.3602514	2.4925967
	M06/BS5	2.0622654	1.9904027	2.3393090	2.4602132
	M06/BS6	2.0543656	1.9868647	2.3372912	2.4577095
CSD ref-code **USIROE**	**Distance (Å)**	**Pt-N4**	**Pt-N11**	**Pt-Cl2**	**Pt-Cl3**
	X-Ray	2.0165777	1.9889958	2.2853507	2.2873804
	B3LYP/BS1	2.0707395	1.9888399	2.3249090	2.3124277
	M06/BS1	2.0753368	1.9913298	2.3199198	2.3080715
	M06/BS3	2.0900499	2.0070067	2.3427199	2.3288594
	M06/BS4	2.0856877	2.0052505	2.3456962	2.3337356
	M06/BS5	2.0869163	1.9995239	2.3275515	2.3158520
	M06/BS6	2.0771855	1.9923494	2.3187464	2.3092099
3c-dmso	**Distance (Å)**	**Pt-N1**	**Pt-N3**	**Pt-C**	**O-H(Ar)**
	X-Ray	1.9815110	2.0692093	2.0187738	2.3730115
	B3LYP/BS1	2.0054755	2.1168696	2.0326425	2.2750508
	M06/BS1	2.0054725	2.1180387	2.0251209	2.3088825
	M06/BS3	2.0094734	2.1403243	2.0249783	2.3303502
	M06/BS4	2.0070347	2.1373136	2.0266382	2.3445129
	M06/BS5	2.0122634	2.1338259	2.0264492	2.3263306
	M06/BS6	2.0061130	2.1191390	2.0263235	2.3187464

Table S2. Second order perturbation theory analysis of Fock matrix in NBO basis for transition structures *trans*-**1/5b** and *cis*-**1/5b,** calculated at (SCRF)M06+D3/BS2//(SCRF)M06/BS1 level. Most significant differences between transition structures *cis*-**1/5b** and *trans*-**1/5b** were found associated with donor-acceptor interactions between a lone pair on the leaving chloride atom and Rydberg orbitals localized at pyridine nitrogen (N3), imine nitrogen (N2), activated carbon (C6), and imine carbon (C12) of the *N*-phenyl hydrazone moiety. For transition structure *trans*-**1/5b**, these interactions provided stabilization energies which were estimated 39-122% higher than the corresponding values for *cis*-**1/5b.**





interaction		*trans*-**1/5b**		*cis*-**1/5b**		Δ
Donor (NBO)	Acceptor (NBO)	E^2_{trans} (kcal/mol)	Distance (Å)	E^2_{cis} (kcal/mol)	Distance (Å)	E^2_{cis}/E^2_{trans} (%)
Cl (LP)	N3 (RY*)	32.8	3.99	22.4	4.25	68
Cl (LP)	N2 (RY*)	31.4	3.43	22.8	3.56	72
Cl (LP)	C6 (RY*)	27.6	3.60	12.4	3.47	45
Cl (LP)	C12 (RY*)	14.8	4.21	8.9	4.43	60
Cl (LP)	C11 (RY*)	8.9	4.80	8.4	5.06	94
Cl (LP)	N1 (RY*)	7.9	3.79	3.5	3.82	44
Cl (LP)	C7 (RY*)	7.5	4.47	2.2	4.73	29
Cl (LP)	C5 (RY*)	4.1	3.99	2.7	4.50	66
Cl (LP)	C1 (RY*)	2.5	3.53	1.7	4.10	68
Cl (LP)	C6-H6 (σ*)	-	-	3.5	2.40	-

LP = Lone pair, RY*= 1-center Ridberg orbital

5.- Crystallographic Study

- Molecular structure and intermolecular interactions for complexes 2e-dmso and 5e.

Figure S5. Graphical representation of the parameters used to describe the π-π stacking interactions.

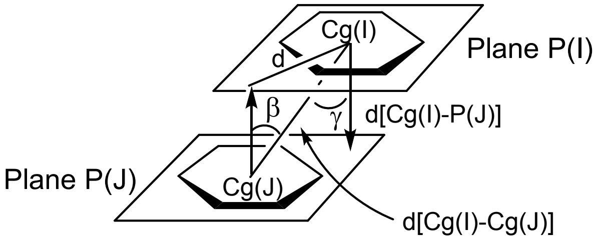


Table S3. Intra- and intermolecular π–π stacking parameters for **2e-dmso** and its Pd(II) analogous and for the trimer **5e**, calculated using the program PLATON. [31]

		d[Cg(I)···Cg(J)][a]	**α**[b]	**β**[c]	**γ**[d]	d[Cg(I)···P(J)][e]	d[Cg(J)···P(I)][f]	d[g]
2e-dmso	ring 2 / pyridazine	3.607(3)	0.0	10.15	10.15	3.55	3.55	0.636
	ring 3 / ring 3	3.599(3)/	0.0	9.4	9.4	3.55	3.55	0.590
IGIHIQ	ring 2 / pyridazine	3.688(4)	0.0	11.6	11.6	3.61	3.61	0.741
Palladium (II) analogous [1]	ring 3 / ring 3	3.689(4)	0.0	11.7	11.7	3.61	3.61	0.747
5e	ring1/ ring3	3.264(8)	2.8	7.7	6.3	3.24	3.23	
	ring2/ ring4	3.271(9)	2.1	7.8	9.8	3.22	3.24	
	pyridazine / phenyl	3.425(8)	0.0	18.7	18.7	3.24	3.24	
	pyridazine / phenyl	3.406(10)	2.5	20.3	18.8	3.22	3.19	
	pyridazine / pyridazine	3.503(9)	4.9	16.6	17.6	3.34	3.36	
	pyridazine / phenyl (intermolecular)	3.506(9)	1.7	16.0	16.9	3.35	3.37	

a Centroid-centroid distance. b Dihedral angle between the ring planes. c Angle between the centroid vector Cg(I)···Cg(J) and the normal to the plane I. d Angle between the centroid vector Cg(I)···Cg(J) and the normal to the plane J. e Perpendicular distance of Cg(I) on ring plane J. f Perpendicular distance of Cg(J) on ring plane I. g Slippage; distance between Cg(I) and perpendicular projection of Cg(J) on Ring I; parallel displacement between ring centroids from a perfect face-to-face alignment.

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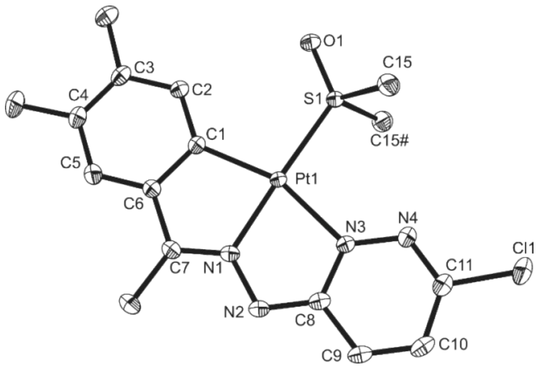
[31] A. L. Spek. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: The Netherlands, 2001.

Structure of 2e-dmso.

The asymmetric unit contains one-half molecule of the complex with all its non-hydrogen atoms, except the dmso methyl, lying in the (0 4 0) crystallographic mirror plane. In the molecule the platinum atom is bonded in a slightly distorted square-planar geometry to the C(1) carbon atom of the phenyl ring, the N(1) and the pyridazine N(3) nitrogen atoms, and to the S(1) sulphur atom of the coordinated dmso ligand. The angles between adjacent atoms in the coordination sphere of platinum are close to the expected value of 90° with the most noticeable distortions corresponding to the N(1)-Pt(1)-N(3) angle of 77.9(2)° and the C(1)-Pt(1)-S(1) angle of 101.0(2)°. The sum of the angles about platinum is approximately 360°.

Figure S6. Molecular structure of [Pt{3,4-Me$_2$-C$_6$H$_2$C(Me)=NN(4’-Cl-C$_4$H$_2$N$_2$)}((CH$_3$)$_2$S=O)], **2e-dmso**. Hydrogen atoms have been omitted for clarity.



The Pt(1)-N(1) and Pt(1)-C(1) bond distances [1.981(5) and 2.018(6) Å, respectively] are somewhat shorter than the value predicted from the sum of their covalent radii [2.07 and 2.09 Å, respectively] [32] indicating that partial double bond character must be present.

The Pt(1)-N(3), 2.069(2) Å, bond length is longer than the Pt(1)-N(1) distance, by the greater *trans* influence of the C(1) carbon atom as compared to the S(1) Sulphur.

The geometry around the platinum atom [Pt(1), C(1), N(1), N(3), S(1), plane 1] is planar (r.m.s. = 0.000). The metallated ring [Pt(1), C(1), C(6), C(7), N(1), ring 2] and the coordination ring [Pt(1), N(1), N(2), C(8), N(3), ring 3] are also planar (r.m.s. = 0.00). Plane 1 and rings 2 and 3, the metallated phenyl ring and the pyridazine ring are coplanar.

π-π interactions, playing an important role in the crystal packing, between the parallel pyridazine groups and the cyclometallated [Pt(1), C(1), C(6), C(7), N(1), ring 2] rings (separation distance of the ring centroids is 3.607(3) Å) were found.

The metal chelate rings [Pt(1), N(1), N(2), C(8), N(3), ring 3] of neighbouring molecules were also parallel and within the distance expected for a π-π “slipped stacking” interaction (separation between ring centroids 3.599(3) Å). A summary of the structural parameters used to describe the π-π interactions are shown in table S3. The fact that we have previously observed similar interactions in an analogous complex with Pd(II) instead of Pt(II) as central atom is indicative that the intermolecular interactions do not depend on the metal atom.

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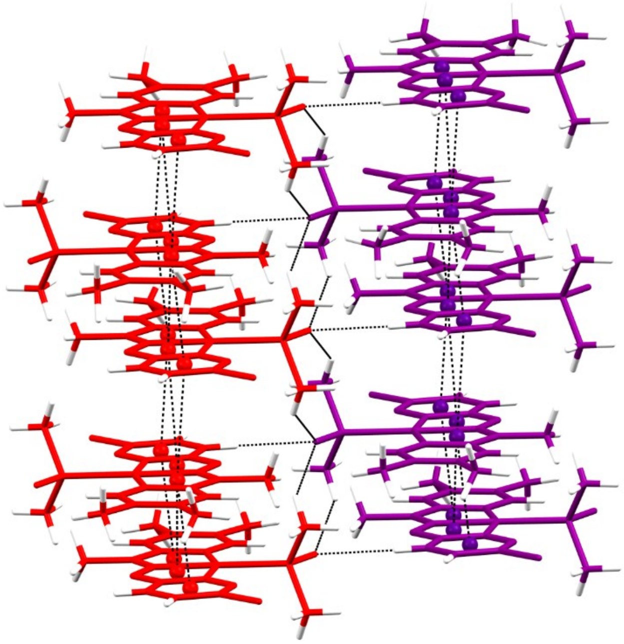
[32] B. Cordero, V. Gómez, A. E. Platero-Prats, M Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.

As a consequence of the intermolecular interactions, the molecules are stacked in a parallel disposition and arranged in rows parallel to the *a* crystallographic axis (see Figure S7). The molecules of different rows show weak C-H···O hydrogen bonds between one dmso oxygen and the H9 hydrogen atom of one pyridazine ring and H15 hydrogens from the dimethyl sulfoxide methyls.

Figure S7. Crystal packing diagram viewed nearly perpendicular to the *b* axis showing the disposition of [Pt{3,4-$(Me)_2C_6H_2C(Me)=NN(4'-ClC_4H_2N_2)$}$[(CH_3)_2S=O]$], **2e-dmso**, molecules in rows.



- Structural evidence of metalloaromaticity in 2e-dmso.

Ghedini *et al* [33] have studied the aromaticity of metallacycles according to structural parameters, in particular the relationship between the "aromaticity" in five membered palladium (II) [C,N] metallacycles which involved conjugated double bonds, and the structural parameters V and HOMA, typically used in organic heterocycles. These parameters are based exclusively in bond distances within the metallacycle. The authors showed the clear relationship between those "aromaticity" parameters and the planarity of the metallacycle. They have also found a correlation between the Pd-N bond length within the metallacycle and the aromatic character of the ring. They also observed that coordination to the metal centre alter all the bond distances within the metallacycle, lengthening double bonds and shortening single ones (see Figure S8).

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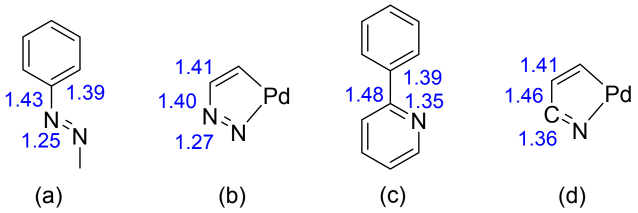
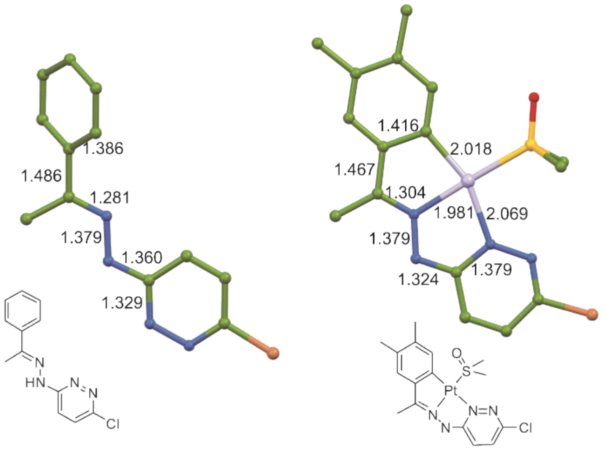
[33] A. Crispini, M. Ghedini, *J. Chem. Soc., Dalton Trans.*, 1997, 75-80.

Figure S8. Variation of bond lengths (in Å) after the formation of the metallacycle in typical metallacyclic rings. (a) and (b) show the usual bond distances in uncoordinated azobenzenes and phenyl pyridines, respectively, (b) and (d), show the variation of the distances within the metallacycle after coordination.



Complex **2e-dmso** complies with the Ghedini parameters: planarity of the system, relatively short Pt-N and Pt-C bond distances, *vide supra*, and modification of ligand bond distances (for comparative reasons the bond lengths from X-ray diffraction analyses of a ligand similar to **e** [34] are given in Figure S9) after coordination. Thus, the two fused metallacycle rings in **2e-dmso** must have, at some degree, aromatic character.

Figure S9. Bond lengths (Å) in complex **2e-dmso** and a ligand similar to **e**, shown with comparative purpose.



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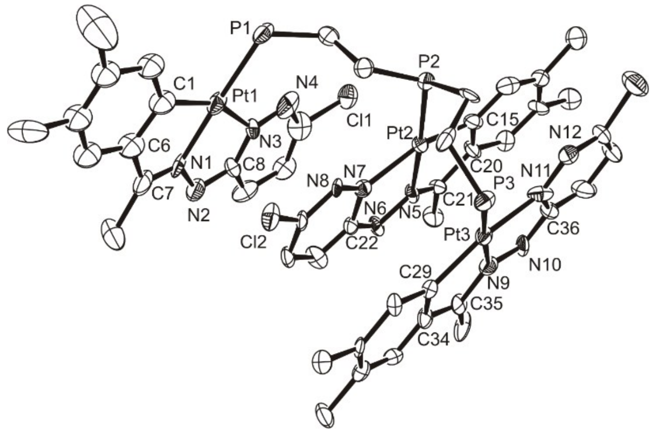
[34] A. Q. Ather, M. N. Tahir, M. A. Khan, M. M. Athar, *Acta Crystallogr.* Sect. E. Struct. Rep. Online 2010, **66**, o2107.

Crystal structure of 5e

Figure S10. Molecular structure of the cation of **5e**. Hydrogen atoms and phosphine phenyl rings have been omitted for clarity reasons. Ellipsoids drawn at 40% of probability.



The crystal structure comprises one cation, three chloride anions and 2.5 solvent water molecules per asymmetric unit. Each platinum atom is bonded, in a slightly distorted square-planar geometry to four atoms: one carbon atom of the phenyl ring and two nitrogen atoms, one from the C=N group and another from the heterocyclic ring. The fourth coordination position is occupied by one phosphorus atom from the $(Ph_2PCH_2CH_2)_2PPh$ (triphos) ligand which is acting as a bridging ligand binding three [Pt(C,N,N')] moieties. The angles between adjacent atoms in the coordination sphere of platinum are close to the expected value of 90°. All bond distances are within expected values with allowance for the *trans* influence of the phenyl carbon and phosphorus atoms.[35]

The presence of an aromatic system constituted by the fusion of the heterocyclic and phenyl rings, plus two five-membered, the metallacycle and the coordination rings, indicated that, in this type of structures, π-π interactions can play an important role in controlling the crystal packing, *vide supra*. Consequently the cyclometallated moieties bonded to Pt(2) and Pt(3) adopt an almost anti-parallel disposition with a distance between the platinum atoms of 3.392(1) Å. This arrangement is stabilized by π-π stacking interactions between the metallated phenyls and the heterocyclic rings (distance between the ring centroids of approximately 3.4 Å) displaying the so-called "slipped stacking". On the other hand, the centroid distances between the cyclometallated rings [Pt(2), N(5), C(15), C(20), C(21): ring 1, Pt(3), N(9), C(29), C(34), C(35): ring 2] and the coordination rings [Pt(2), N(5), N(6), N(7), C(22): ring 3, Pt(3), N(9), N(10), N(11), C(6): ring 4] are within the values expected for π-π stacked rings [distance ring 1-ring 3 = 3.264(8) Å, distance ring 2-ring 4 = 3.271(9) Å]. This observation supports the existence of some degree of "metalloaromaticity" due to active charge delocalization (vide supra).

Similar "slipped stacking"π-π stacking interactions have also been found between the pyridazine rings bonded to Pt(1) and Pt(3), with a distance between the ring centroids of 3.503(9) Å (see Figure S11).

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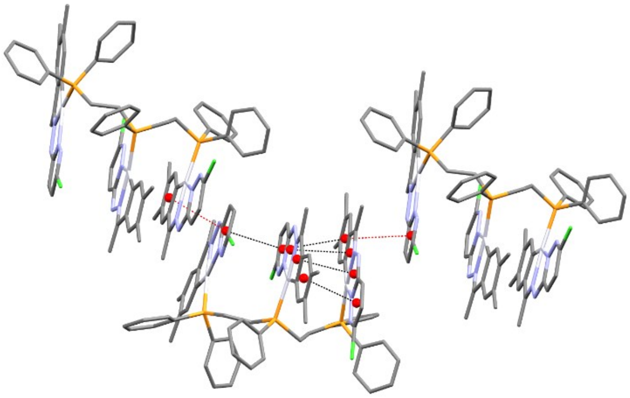
35 (a) W. Lu, N. Zhu, C-M. Che, *Chem. Commun.*, 2002, 900-901; (b) W- Lu, M. C. W. Chan, N. Zhu, C. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.*, 2004, **126**, 7639-7651; (c) P. Shao, W. Sun, *Inorg. Chem.*, 2007, **46**, 8603-8612.

Figure S11. View of the intermolecular (in red) and intramolecular (in black) π,π-stacking interactions within the crystal of **5e**, dashed lines link the centroids of the rings involved in each stacking interaction



Within the crystal, the cyclometallated ligands also adopt a parallel disposition, stabilized by intermolecular π-π stacking between the pyridazine ring bonded to Pt(1) and the phenyl ring bonded to Pt(3) [distance between centroids of 3.506(9) Å]

X-ray crystallographic study

A Green plate-like crystal was obtained by recrystallization from a dimethyl sulfoxide solution of **1e** (crystal size 0.20 x 0.20 x 0.08 mm) and a colorless prismatic crystal of **5e** (crystal size 0.29 x 0.25 x 0.10 mm) by recrystallization from a chloroform solution

Crystal data.

2e-dmso: $C_{16}H_{19}ClN_4OPtS$, M = 545.95, Monoclinic, space group $P2_1/m$, a = 10.197(5) Å, b = 7.101(5) Å, c = 12.014(5) Å, β = 99.124(2)° V = 858(1) Å^3, Z = 2, $D_{calc.}$ = 2.111 g/cm^3, $F(000)$ = 524, λ(Mo-K_α) = 0.71073 Å and μ = 8.456 cm^{-1}. CCDC 1536508 and the Supplementary Information contain crystallographic data for **2e-dmso.**

5e: $C_{76}H_{80}Cl_6N_{12}O_{2.5}P_3Pt_3$, M = 2092.4, Orthorhombic, space group $Pca2_1$, a = 19.819(5) Å, b = 15.689(5) Å, c = 29.119(5) Å, V = 9054(4) Å^3, Z = 4, $D_{calc.}$ = 1.535 g/cm^3, $F(000)$ = 4084, λ(Mo-K_α) = 0.71073 Å and μ = 4.901 cm^{-1}. CCDC 1536509 and the Supplementary Information contain crystallographic data for **5e**.

Three-dimensional, room temperature X-ray data were collected on a Bruker X8 Apex diffractometer using graphite-monochromated Mo Ka radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. In the structure of **5e** The H2A, H6 and H10A hydrogen atoms, corresponding to the C=N-N(H)- group, were initially located in a Fourier difference map, however they were refined in riding mode to achieve the final convergence in the refinement.

In the crystal of **5e** two full occupancy water solvent molecules (one of them disordered over two positions) and one with occupancy of 0.5 were located in the asymmetric unit, however peaks of relatively low residual density remained in the crystal and no reasonably model could be used to refine them as a disordered solvent molecule. A search for solvent-accessible voids in the crystal using PLATON- SQUEEZE [36] showed four voids with an approximate volume of 350 Å^3 giving a total potential solvent volume of 1480 Å^3 per cell (16.3 % of the cell volume). The number of electrons found in each void was approximately 28 and the estimated volume per atom 100 Å^3. This indicates that the void is only partially occupied and that the original contents had probably disappeared by the time the crystal was used for data collection, without collapsing the structure.

Refinement converged at a final R = 0.0257 and 0.0634 (for **2e-dmso** and **5e**, respectively, reflections with $I > 2\sigma(I)$, F) and wR_2 = 0.0587 and 0.1504 (for **1e-dmso** and **5e**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms (except those corresponding to the water solvent molecules in the crystal of **5e** which were refined isotropically).

The structure solution and refinement were carried out using the program package SHELX-97.[37]

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36 A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, University of Utrecht: The Netherlands, 2001.

37 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.

Table S4. Crystal data and structure refinement for **2e-dmso**.

Empirical formula	$C_{16}H_{19}ClN_4OPtS$	
Formula weight	545.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/m	
Unit cell dimensions	a = 10.197(5) Å	α= 90°.
	b = 7.101(5) Å	β= 99.124(2)°.
	c = 12.014(3) Å	γ = 90°.
Volume	858.9(8) Å^3	
Z	2	
Density (calculated)	2.111 Mg/m^3	
Absorption coefficient	8.456 mm^{-1}	
F(000)	524	
Crystal size	0.200 x 0.200 x 0.080 mm^3	
Theta range for data collection	2.023 to 26.393°.	
Index ranges	-12<=h<=12, -8<=k<=8, -14<=l<=15	
Reflections collected	13106	
Independent reflections	1902 [R(int) = 0.0502]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5181 and 0.3325	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1902 / 0 / 146	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0558	
R indices (all data)	R1 = 0.0326, wR2 = 0.0587	
Largest diff. peak and hole	2.689 and -1.170 e.Å^{-3}	

Table S5. Crystal data and structure refinement for **5e**.

Empirical formula	$C_{76}H_{80}Cl_{6}N_{12}O_{2.50}P_{3}\,Pt_{3}$	
Formula weight	2092.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P ca21	
Unit cell dimensions	a = 19.819(5) Å	α= 90°.
	b = 15.689(5) Å	β= 90°.
	c = 29.119(5) Å	γ = 90°.
Volume	9054(4) $Å^3$	
Z	4	
Density (calculated)	1.535 Mg/m^3	
Absorption coefficient	4.901 mm^{-1}	
F(000)	4084	
Crystal size	0.270 x 0.250 x 0.100 mm^3	
Theta range for data collection	2.055 to 28.337°.	
Index ranges	-26<=h<=26, -20<=k<=20, -18<=l<=37	
Reflections collected	77741	
Independent reflections	16475 [R(int) = 0.0617]	
Completeness to theta = 25.242°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.690 and 0.346	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16475 / 158 / 914	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.1443	
R indices (all data)	R1 = 0.0775, wR2 = 0.1504	
Absolute structure parameter	0.082(13)	
Largest diff. peak and hole	2.221 and -2.809 e.$Å^{-3}$	

Table S6. Selected bond lengths (Å) and angles (°) for complexes **2e-dmso** and **5e**.

	2e-dmso	5e
Pt(1)-C(1)	2.02(1)	2.01(2)
Pt(1)-N(1)	1.98(1)	1.98(2)
Pt(1)-N(3)	2.07(1)	2.15(2)
Pt(1)-S(1)	2.214(2)	
Pt(1)-P(1)		2.25(1)
Pt(2)-C(15)		2.01(3)
Pt(2)-N(5)		2.02(1)
Pt(2)-N(7)		2.07(2)
Pt(2)-P(2)		2.24(1)
Pt(3)-C(29)		2.01(2)
Pt(3)-N(9)		2.02(1)
Pt(3)-N(11)		2.08(2)
Pt(3)-P(3)		2.25(1)
C(1)-Pt(1)-N(1)	81.1(2)	79.3(8)
N(1)-Pt(1)-N(3)	77.9(2)	78.2(7)
N(3)-Pt(1)-S(1)	100.0(1)	
S(1)-Pt(1)-C(1)	100.1(2)	
N(3)-Pt(1)-P(1)		102.1(5)
P(1)-Pt(1)-C(1)		100.5(6)
C(15)-Pt(2)-N(5)		81.8(7)
N(5)-Pt(2)-N(7)		77.4(6)
N(7)-Pt(2)-P(2)		104.0(4)
P(2)-Pt(2)-C(15)		97.0(5)
C(29)-Pt(3)-N(9)		81.0(7)
N(9)-Pt(3)-N(11)		78.3(6)
N(11)-Pt(3)-P(3)		99.6(4)
P(3)-Pt(3)-C(29)		101.0(5)

6. Energies of the calculated structures (Gaussian09 output format).

$[PtCl_4]^{2-}$

```
 ---------------------------------------------------------------------
 (SCRF)M06/BS1 (scrf=(solvent=1-butanol))
 Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                           0.004612 (Hartree/Particle)
 Thermal correction to Energy=                    0.014917
 Thermal correction to Enthalpy=                  0.016099
 Thermal correction to Gibbs Free Energy=        -0.041859
 Sum of electronic and zero-point Energies=          -1960.714804
 Sum of electronic and thermal Energies=             -1960.704498
 Sum of electronic and thermal Enthalpies=           -1960.703317
 Sum of electronic and thermal Free Energies=        -1960.761274
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
  SCF Done:  E(RM06) =  -1960.77580305     A.U. after   11 cycles
 ---------------------------------------------------------------------
```

$[PtCl_3]^-$

```
 ---------------------------------------------------------------------
 (SCRF)M06/BS1 (scrf=(solvent=1-butanol))
 Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                           0.002903 (Hartree/Particle)
 Thermal correction to Energy=                    0.011133
 Thermal correction to Enthalpy=                  0.012315
 Thermal correction to Gibbs Free Energy=        -0.040850
 Sum of electronic and zero-point Energies=          -1500.315375
 Sum of electronic and thermal Energies=             -1500.307145
 Sum of electronic and thermal Enthalpies=           -1500.305964
 Sum of electronic and thermal Free Energies=        -1500.359129
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
  SCF Done:  E(RM06) =  -1500.36075986     A.U. after   13 cycles
 ---------------------------------------------------------------------
```

Cl^-

```
 ---------------------------------------------------------------------
 (SCRF)M06/BS1 (scrf=(solvent=1-butanol))
 Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                           0.000000 (Hartree/Particle)
 Thermal correction to Energy=                    0.001773
 Thermal correction to Enthalpy=                  0.002954
 Thermal correction to Gibbs Free Energy=        -0.019465
 Sum of electronic and zero-point Energies=           -460.350302
 Sum of electronic and thermal Energies=              -460.348529
 Sum of electronic and thermal Enthalpies=            -460.347348
 Sum of electronic and thermal Free Energies=         -460.369767
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
  SCF Done:  E(RM06) =  -460.374669851     A.U. after    8 cycles
 ---------------------------------------------------------------------
```

HCl

```
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS1 (scrf=(solvent=1-butanol))
 Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                           0.006633 (Hartree/Particle)
 Thermal correction to Energy=                    0.009588
 Thermal correction to Enthalpy=                  0.010769
 Thermal correction to Gibbs Free Energy=        -0.016706
 Sum of electronic and zero-point Energies=           -460.785621
 Sum of electronic and thermal Energies=              -460.782666
 Sum of electronic and thermal Enthalpies=            -460.781484
 Sum of electronic and thermal Free Energies=         -460.808959
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
  SCF Done:  E(RM06) =  -460.807216962     A.U. after    8 cycles
 ---------------------------------------------------------------------
```

BuOH

```
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS1 (scrf=(solvent=1-butanol))
 Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
 Zero-point correction=                           0.135830 (Hartree/Particle)
 Thermal correction to Energy=                    0.145624
 Thermal correction to Enthalpy=                  0.146805
 Thermal correction to Gibbs Free Energy=         0.096160
 Sum of electronic and zero-point Energies=           -233.365449
 Sum of electronic and thermal Energies=              -233.355655
 Sum of electronic and thermal Enthalpies=            -233.354473
 Sum of electronic and thermal Free Energies=         -233.405118
 ---------------------------------------------------------------------
 (SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
SCF Done:  E(RM06) =  -233.586672977     A.U. after   11 cycles
 ---------------------------------------------------------------------
```

Ligand a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.224240 (Hartree/Particle)
Thermal correction to Energy=                    0.246965
Thermal correction to Enthalpy=                  0.248147
Thermal correction to Gibbs Free Energy=         0.163168
Sum of electronic and zero-point Energies=          -1126.344456
Sum of electronic and thermal Energies=             -1126.321731
Sum of electronic and thermal Enthalpies=           -1126.320549
Sum of electronic and thermal Free Energies=        -1126.405528
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1126.77018559     A.U. after   14 cycles
---------------------------------------------------------------------
```

a/3a$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228507 (Hartree/Particle)
Thermal correction to Energy=                    0.260614
Thermal correction to Enthalpy=                  0.261795
Thermal correction to Gibbs Free Energy=         0.152231
Sum of electronic and zero-point Energies=          -2626.669895
Sum of electronic and thermal Energies=             -2626.637788
Sum of electronic and thermal Enthalpies=           -2626.636607
Sum of electronic and thermal Free Energies=        -2626.746171
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2627.14426494     A.U. after   24 cycles
---------------------------------------------------------------------
```

3a$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.229408 (Hartree/Particle)
Thermal correction to Energy=                    0.261884
Thermal correction to Enthalpy=                  0.263065
Thermal correction to Gibbs Free Energy=         0.154803
Sum of electronic and zero-point Energies=          -2626.692402
Sum of electronic and thermal Energies=             -2626.659927
Sum of electronic and thermal Enthalpies=           -2626.658745
Sum of electronic and thermal Free Energies=        -2626.767007
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2627.16558494     A.U. after   19 cycles
---------------------------------------------------------------------
```

3/4a$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228850 (Hartree/Particle)
Thermal correction to Energy=                    0.260650
Thermal correction to Enthalpy=                  0.261832
Thermal correction to Gibbs Free Energy=         0.154087
Sum of electronic and zero-point Energies=          -2626.672547
Sum of electronic and thermal Energies=             -2626.640747
Sum of electronic and thermal Enthalpies=           -2626.639566
Sum of electronic and thermal Free Energies=        -2626.747310
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2627.14556543     A.U. after   23 cycles
---------------------------------------------------------------------
```

4a$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.230036 (Hartree/Particle)
Thermal correction to Energy=                    0.262382
Thermal correction to Enthalpy=                  0.263564
Thermal correction to Gibbs Free Energy=         0.154934
Sum of electronic and zero-point Energies=          -2626.706221
Sum of electronic and thermal Energies=             -2626.673875
Sum of electronic and thermal Enthalpies=           -2626.672693
Sum of electronic and thermal Free Energies=        -2626.781323
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2627.18132819     A.U. after   18 cycles
---------------------------------------------------------------------
```

4/1a$^-$

```
---------------------------------------------------------------------
```

```
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Zero-point correction=                           0.230495 (Hartree/Particle)
Thermal correction to Energy=                    0.261689
Thermal correction to Enthalpy=                  0.262870
Thermal correction to Gibbs Free Energy=         0.157048
Sum of electronic and zero-point Energies=          -2626.677851
Sum of electronic and thermal Energies=             -2626.646658
Sum of electronic and thermal Enthalpies=           -2626.645476
Sum of electronic and thermal Free Energies=        -2626.751298
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2627.15381237     A.U. after   19 cycles
---------------------------------------------------------------------
```

1a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.230310 (Hartree/Particle)
Thermal correction to Energy=                    0.259409
Thermal correction to Enthalpy=                  0.260591
Thermal correction to Gibbs Free Energy=         0.161085
Sum of electronic and zero-point Energies=          -2166.349831
Sum of electronic and thermal Energies=             -2166.320732
Sum of electronic and thermal Enthalpies=           -2166.319550
Sum of electronic and thermal Free Energies=        -2166.419055
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.81417584     A.U. after   17 cycles
---------------------------------------------------------------------
```

cis-1/5a$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228683 (Hartree/Particle)
Thermal correction to Energy=                    0.257362
Thermal correction to Enthalpy=                  0.258543
Thermal correction to Gibbs Free Energy=         0.159863
Sum of electronic and zero-point Energies=          -2166.290048
Sum of electronic and thermal Energies=             -2166.261370
Sum of electronic and thermal Enthalpies=           -2166.260188
Sum of electronic and thermal Free Energies=        -2166.358869
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.75425669     A.U. after   18 cycles
---------------------------------------------------------------------
```

trans-1/5a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228238 (Hartree/Particle)
Thermal correction to Energy=                    0.257083
Thermal correction to Enthalpy=                  0.258264
Thermal correction to Gibbs Free Energy=         0.159431
Sum of electronic and zero-point Energies=          -2166.294140
Sum of electronic and thermal Energies=             -2166.265296
Sum of electronic and thermal Enthalpies=           -2166.264114
Sum of electronic and thermal Free Energies=        -2166.362948
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.75821600     A.U. after   19 cycles
---------------------------------------------------------------------
```

trans-5a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228406 (Hartree/Particle)
Thermal correction to Energy=                    0.258134
Thermal correction to Enthalpy=                  0.259316
Thermal correction to Gibbs Free Energy=         0.158195
Sum of electronic and zero-point Energies=          -2166.295538
Sum of electronic and thermal Energies=             -2166.265810
Sum of electronic and thermal Enthalpies=           -2166.264629
Sum of electronic and thermal Free Energies=        -2166.365749
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.76259453     A.U. after   18 cycles
---------------------------------------------------------------------
```

5a$^+$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.228097 (Hartree/Particle)
Thermal correction to Energy=                    0.254566
```

```
Thermal correction to Enthalpy=                  0.255748
Thermal correction to Gibbs Free Energy=         0.164335
Sum of electronic and zero-point Energies=          -1705.928154
Sum of electronic and thermal Energies=             -1705.901685
Sum of electronic and thermal Enthalpies=           -1705.900503
Sum of electronic and thermal Free Energies=        -1705.991915
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1706.37871046     A.U. after   17 cycles
---------------------------------------------------------------------
```

cis-5a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.227088 (Hartree/Particle)
Thermal correction to Energy=                    0.256524
Thermal correction to Enthalpy=                  0.257706
Thermal correction to Gibbs Free Energy=         0.158140
Sum of electronic and zero-point Energies=          -2166.301589
Sum of electronic and thermal Energies=             -2166.272153
Sum of electronic and thermal Enthalpies=           -2166.270971
Sum of electronic and thermal Free Energies=        -2166.370537
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.76503897     A.U. after   17 cycles
---------------------------------------------------------------------
```

5/2a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.224619 (Hartree/Particle)
Thermal correction to Energy=                    0.253407
Thermal correction to Enthalpy=                  0.254589
Thermal correction to Gibbs Free Energy=         0.156373
Sum of electronic and zero-point Energies=          -2166.303771
Sum of electronic and thermal Energies=             -2166.274983
Sum of electronic and thermal Enthalpies=           -2166.273801
Sum of electronic and thermal Free Energies=        -2166.372017
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.76308772     A.U. after   17 cycles
---------------------------------------------------------------------
```

2a

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Zero-point correction=                           0.216649 (Hartree/Particle)
Thermal correction to Energy=                    0.243110
Thermal correction to Enthalpy=                  0.244292
Thermal correction to Gibbs Free Energy=         0.152283
Sum of electronic and zero-point Energies=          -1705.533219
Sum of electronic and thermal Energies=             -1705.506758
Sum of electronic and thermal Enthalpies=           -1705.505576
Sum of electronic and thermal Free Energies=        -1705.597585
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1705.96728858     A.U. after   18 cycles
---------------------------------------------------------------------
```

AcO$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.047712 (Hartree/Particle)
Thermal correction to Energy=                    0.053847
Thermal correction to Enthalpy=                  0.055028
Thermal correction to Gibbs Free Energy=         0.012159
Sum of electronic and zero-point Energies=           -228.340592
Sum of electronic and thermal Energies=              -228.334458
Sum of electronic and thermal Enthalpies=            -228.333276
Sum of electronic and thermal Free Energies=         -228.376145
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -228.576615313     A.U. after   12 cycles
---------------------------------------------------------------------
```

AcOH

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.061500 (Hartree/Particle)
Thermal correction to Energy=                    0.067889
Thermal correction to Enthalpy=                  0.069070
Thermal correction to Gibbs Free Energy=         0.026153
Sum of electronic and zero-point Energies=           -228.916916
Sum of electronic and thermal Energies=              -228.910527
```

```
Sum of electronic and thermal Enthalpies=            -228.909345
Sum of electronic and thermal Free Energies=         -228.952262
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -229.052047896     A.U. after   11 cycles
---------------------------------------------------------------------
```

5ac$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.279292 (Hartree/Particle)
Thermal correction to Energy=                    0.316619
Thermal correction to Enthalpy=                  0.317801
Thermal correction to Gibbs Free Energy=         0.197169
Sum of electronic and zero-point Energies=          -2394.819819
Sum of electronic and thermal Energies=             -2394.782492
Sum of electronic and thermal Enthalpies=           -2394.781310
Sum of electronic and thermal Free Energies=        -2394.901942
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2395.40796959     A.U. after   18 cycles
---------------------------------------------------------------------
```

5/6ac$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.279507 (Hartree/Particle)
Thermal correction to Energy=                    0.315465
Thermal correction to Enthalpy=                  0.316646
Thermal correction to Gibbs Free Energy=         0.202015
Sum of electronic and zero-point Energies=          -2394.792764
Sum of electronic and thermal Energies=             -2394.756806
Sum of electronic and thermal Enthalpies=           -2394.755625
Sum of electronic and thermal Free Energies=        -2394.870256
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2395.37740288     A.U. after   17 cycles
---------------------------------------------------------------------
```

6ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.280915 (Hartree/Particle)
Thermal correction to Energy=                    0.314593
Thermal correction to Enthalpy=                  0.315774
Thermal correction to Gibbs Free Energy=         0.207317
Sum of electronic and zero-point Energies=          -1934.461083
Sum of electronic and thermal Energies=             -1934.427405
Sum of electronic and thermal Enthalpies=           -1934.426224
Sum of electronic and thermal Free Energies=        -1934.534681
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1935.03264425     A.U. after   18 cycles
---------------------------------------------------------------------
```

6/7ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.278995 (Hartree/Particle)
Thermal correction to Energy=                    0.312269
Thermal correction to Enthalpy=                  0.313451
Thermal correction to Gibbs Free Energy=         0.206412
Sum of electronic and zero-point Energies=          -1934.432809
Sum of electronic and thermal Energies=             -1934.399535
Sum of electronic and thermal Enthalpies=           -1934.398354
Sum of electronic and thermal Free Energies=        -1934.505392
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1934.99970291     A.U. after   18 cycles
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
```

7ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.279685 (Hartree/Particle)
Thermal correction to Energy=                    0.313641
Thermal correction to Enthalpy=                  0.314822
Thermal correction to Gibbs Free Energy=         0.205686
Sum of electronic and zero-point Energies=          -1934.432624
```

```
Sum of electronic and thermal Energies=             -1934.398668
Sum of electronic and thermal Enthalpies=           -1934.397486
Sum of electronic and thermal Free Energies=        -1934.506622
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1935.00019086     A.U. after   18 cycles
---------------------------------------------------------------------
```

7/8ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.278814 (Hartree/Particle)
Thermal correction to Energy=                    0.312487
Thermal correction to Enthalpy=                  0.313668
Thermal correction to Gibbs Free Energy=         0.204344
Sum of electronic and zero-point Energies=          -1934.419441
Sum of electronic and thermal Energies=             -1934.385768
Sum of electronic and thermal Enthalpies=           -1934.384586
Sum of electronic and thermal Free Energies=        -1934.493911
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1934.98623435     A.U. after   18 cycles
---------------------------------------------------------------------
```

8ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.278623 (Hartree/Particle)
Thermal correction to Energy=                    0.313530
Thermal correction to Enthalpy=                  0.314712
Thermal correction to Gibbs Free Energy=         0.199229
Sum of electronic and zero-point Energies=          -1934.418645
Sum of electronic and thermal Energies=             -1934.383738
Sum of electronic and thermal Enthalpies=           -1934.382557
Sum of electronic and thermal Free Energies=        -1934.498039
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1934.98617547     A.U. after   18 cycles
---------------------------------------------------------------------
```

8/9ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.278754 (Hartree/Particle)
Thermal correction to Energy=                    0.312475
Thermal correction to Enthalpy=                  0.313657
Thermal correction to Gibbs Free Energy=         0.202723
Sum of electronic and zero-point Energies=          -1934.418760
Sum of electronic and thermal Energies=             -1934.385039
Sum of electronic and thermal Enthalpies=           -1934.383857
Sum of electronic and thermal Free Energies=        -1934.494791
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1934.98902916     A.U. after   18 cycles
---------------------------------------------------------------------
```

9ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.278218 (Hartree/Particle)
Thermal correction to Energy=                    0.312860
Thermal correction to Enthalpy=                  0.314042
Thermal correction to Gibbs Free Energy=         0.200736
Sum of electronic and zero-point Energies=          -1934.437482
Sum of electronic and thermal Energies=             -1934.402840
Sum of electronic and thermal Enthalpies=           -1934.401658
Sum of electronic and thermal Free Energies=        -1934.514964
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1935.00322787     A.U. after   19 cycles
---------------------------------------------------------------------
```

9/2ac

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.272089 (Hartree/Particle)
Thermal correction to Energy=                    0.306019
Thermal correction to Enthalpy=                  0.307201
Thermal correction to Gibbs Free Energy=         0.195865
Sum of electronic and zero-point Energies=          -1934.421791
Sum of electronic and thermal Energies=             -1934.387860
Sum of electronic and thermal Enthalpies=           -1934.386678
Sum of electronic and thermal Free Energies=        -1934.498015
```

```
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1934.97819945     A.U. after   18 cycles
---------------------------------------------------------------------
```

Ligand b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.233497 (Hartree/Particle)
Thermal correction to Energy=                    0.254677
Thermal correction to Enthalpy=                  0.255858
Thermal correction to Gibbs Free Energy=         0.175374
Sum of electronic and zero-point Energies=            -666.739929
Sum of electronic and thermal Energies=               -666.718749
Sum of electronic and thermal Enthalpies=             -666.717567
Sum of electronic and thermal Free Energies=          -666.798052
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -667.164691563     A.U. after   14 cycles
---------------------------------------------------------------------
```

b/3b^{-}

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237519 (Hartree/Particle)
Thermal correction to Energy=                    0.268239
Thermal correction to Enthalpy=                  0.269421
Thermal correction to Gibbs Free Energy=         0.162793
Sum of electronic and zero-point Energies=           -2167.064876
Sum of electronic and thermal Energies=              -2167.034156
Sum of electronic and thermal Enthalpies=            -2167.032974
Sum of electronic and thermal Free Energies=         -2167.139602
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2167.53776849     A.U. after   19 cycles
---------------------------------------------------------------------
```

3b^{-}

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.238474 (Hartree/Particle)
Thermal correction to Energy=                    0.269455
Thermal correction to Enthalpy=                  0.270636
Thermal correction to Gibbs Free Energy=         0.165508
Sum of electronic and zero-point Energies=           -2167.087661
Sum of electronic and thermal Energies=              -2167.056679
Sum of electronic and thermal Enthalpies=            -2167.055498
Sum of electronic and thermal Free Energies=         -2167.160626
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2167.55935689     A.U. after   19 cycles
---------------------------------------------------------------------
```

3/4b^{-}

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237882 (Hartree/Particle)
Thermal correction to Energy=                    0.268226
Thermal correction to Enthalpy=                  0.269408
Thermal correction to Gibbs Free Energy=         0.165077
Sum of electronic and zero-point Energies=           -2167.067539
Sum of electronic and thermal Energies=              -2167.037195
Sum of electronic and thermal Enthalpies=            -2167.036013
Sum of electronic and thermal Free Energies=         -2167.140344
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2167.53949063     A.U. after   20 cycles
---------------------------------------------------------------------
```

4b^{-}

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.239164 (Hartree/Particle)
Thermal correction to Energy=                    0.269890
Thermal correction to Enthalpy=                  0.271072
Thermal correction to Gibbs Free Energy=         0.166079
Sum of electronic and zero-point Energies=           -2167.100728
Sum of electronic and thermal Energies=              -2167.070001
Sum of electronic and thermal Enthalpies=            -2167.068820
Sum of electronic and thermal Free Energies=         -2167.173813
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
```

```
 SCF Done:  E(RM06) =  -2167.57278868     A.U. after   18 cycles
---------------------------------------------------------------------
```

4/1b$^-$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.239548 (Hartree/Particle)
Thermal correction to Energy=                    0.269196
Thermal correction to Enthalpy=                  0.270378
Thermal correction to Gibbs Free Energy=         0.169260
Sum of electronic and zero-point Energies=          -2167.073834
Sum of electronic and thermal Energies=             -2167.044186
Sum of electronic and thermal Enthalpies=           -2167.043004
Sum of electronic and thermal Free Energies=        -2167.144123
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2167.54824225     A.U. after   19 cycles
---------------------------------------------------------------------
```

1b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.240042 (Hartree/Particle)
Thermal correction to Energy=                    0.267299
Thermal correction to Enthalpy=                  0.268481
Thermal correction to Gibbs Free Energy=         0.173464
Sum of electronic and zero-point Energies=          -1706.745539
Sum of electronic and thermal Energies=             -1706.718283
Sum of electronic and thermal Enthalpies=           -1706.717101
Sum of electronic and thermal Free Energies=        -1706.812117
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.20906442     A.U. after   17 cycles
---------------------------------------------------------------------
```

cis-1/5b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237896 (Hartree/Particle)
Thermal correction to Energy=                    0.265077
Thermal correction to Enthalpy=                  0.266259
Thermal correction to Gibbs Free Energy=         0.170981
Sum of electronic and zero-point Energies=          -1706.688316
Sum of electronic and thermal Energies=             -1706.661135
Sum of electronic and thermal Enthalpies=           -1706.659953
Sum of electronic and thermal Free Energies=        -1706.755231
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.15090747     A.U. after   19 cycles
---------------------------------------------------------------------
```

trans-1/5b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237431 (Hartree/Particle)
Thermal correction to Energy=                    0.264741
Thermal correction to Enthalpy=                  0.265923
Thermal correction to Gibbs Free Energy=         0.171360
Sum of electronic and zero-point Energies=          -1706.692921
Sum of electronic and thermal Energies=             -1706.665611
Sum of electronic and thermal Enthalpies=           -1706.664429
Sum of electronic and thermal Free Energies=        -1706.758993
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.15470831     A.U. after   19 cycles
---------------------------------------------------------------------
```

trans-5b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237197 (Hartree/Particle)
Thermal correction to Energy=                    0.265586
Thermal correction to Enthalpy=                  0.266767
Thermal correction to Gibbs Free Energy=         0.168833
Sum of electronic and zero-point Energies=          -1706.694938
Sum of electronic and thermal Energies=             -1706.666549
Sum of electronic and thermal Enthalpies=           -1706.665368
Sum of electronic and thermal Free Energies=        -1706.763302
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.15948958     A.U. after   19 cycles
---------------------------------------------------------------------
```

5b$^+$

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237738 (Hartree/Particle)
Thermal correction to Energy=                    0.262683
Thermal correction to Enthalpy=                  0.263865
Thermal correction to Gibbs Free Energy=         0.176088
Sum of electronic and zero-point Energies=          -1246.328058
Sum of electronic and thermal Energies=             -1246.303113
Sum of electronic and thermal Enthalpies=           -1246.301932
Sum of electronic and thermal Free Energies=        -1246.389709
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1246.77725394     A.U. after   17 cycles
---------------------------------------------------------------------
```

cis-5b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.237161 (Hartree/Particle)
Thermal correction to Energy=                    0.264939
Thermal correction to Enthalpy=                  0.266120
Thermal correction to Gibbs Free Energy=         0.170753
Sum of electronic and zero-point Energies=          -1706.699612
Sum of electronic and thermal Energies=             -1706.671835
Sum of electronic and thermal Enthalpies=           -1706.670653
Sum of electronic and thermal Free Energies=        -1706.766021
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.16297080     A.U. after   17 cycles
---------------------------------------------------------------------
```

5/2b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.233118 (Hartree/Particle)
Thermal correction to Energy=                    0.260371
Thermal correction to Enthalpy=                  0.261553
Thermal correction to Gibbs Free Energy=         0.167705
Sum of electronic and zero-point Energies=          -1706.702918
Sum of electronic and thermal Energies=             -1706.675664
Sum of electronic and thermal Enthalpies=           -1706.674483
Sum of electronic and thermal Free Energies=        -1706.768331
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1707.15908534     A.U. after   17 cycles
---------------------------------------------------------------------
```

2b

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.225673 (Hartree/Particle)
Thermal correction to Energy=                    0.250633
Thermal correction to Enthalpy=                  0.251815
Thermal correction to Gibbs Free Energy=         0.163070
Sum of electronic and zero-point Energies=          -1245.927965
Sum of electronic and thermal Energies=             -1245.903005
Sum of electronic and thermal Enthalpies=           -1245.901823
Sum of electronic and thermal Free Energies=        -1245.990567
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1246.36071395     A.U. after   18 cycles
---------------------------------------------------------------------
```

1c

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.230998 (Hartree/Particle)
Thermal correction to Energy=                    0.259857
Thermal correction to Enthalpy=                  0.261038
Thermal correction to Gibbs Free Energy=         0.161674
Sum of electronic and zero-point Energies=          -2166.350145
Sum of electronic and thermal Energies=             -2166.321286
Sum of electronic and thermal Enthalpies=           -2166.320104
Sum of electronic and thermal Free Energies=        -2166.419468
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.81484135     A.U. after   17 cycles
---------------------------------------------------------------------
```

trans-1/5c

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                            0.227897 (Hartree/Particle)
Thermal correction to Energy=                     0.256845
Thermal correction to Enthalpy=                   0.258026
Thermal correction to Gibbs Free Energy=          0.158890
Sum of electronic and zero-point Energies=           -2166.296507
Sum of electronic and thermal Energies=              -2166.267559
Sum of electronic and thermal Enthalpies=            -2166.266378
Sum of electronic and thermal Free Energies=         -2166.365514
-----------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.75906773     A.U. after   17 cycles
-----------------------------------------------------------------------
```

cis-1/5c

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                            0.228572 (Hartree/Particle)
Thermal correction to Energy=                     0.257234
Thermal correction to Enthalpy=                   0.258415
Thermal correction to Gibbs Free Energy=          0.160339
Sum of electronic and zero-point Energies=           -2166.291624
Sum of electronic and thermal Energies=              -2166.262962
Sum of electronic and thermal Enthalpies=            -2166.261780
Sum of electronic and thermal Free Energies=         -2166.359857
-----------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2166.75537071     A.U. after   18 cycles
-----------------------------------------------------------------------
```

5c$^+$

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                            0.228293 (Hartree/Particle)
Thermal correction to Energy=                     0.254889
Thermal correction to Enthalpy=                   0.256071
Thermal correction to Gibbs Free Energy=          0.164056
Sum of electronic and zero-point Energies=           -1705.931042
Sum of electronic and thermal Energies=              -1705.904446
Sum of electronic and thermal Enthalpies=            -1705.903264
Sum of electronic and thermal Free Energies=         -1705.995280
-----------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -1706.38117680     A.U. after   17 cycles
-----------------------------------------------------------------------
```

1d

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                            0.220825 (Hartree/Particle)
Thermal correction to Energy=                     0.251651
Thermal correction to Enthalpy=                   0.252833
Thermal correction to Gibbs Free Energy=          0.148367
Sum of electronic and zero-point Energies=           -2625.952828
Sum of electronic and thermal Energies=              -2625.922001
Sum of electronic and thermal Enthalpies=            -2625.920819
Sum of electronic and thermal Free Energies=         -2626.025286
-----------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2626.41789747     A.U. after   18 cycles
-----------------------------------------------------------------------
```

trans-1/5d

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                            0.218164 (Hartree/Particle)
Thermal correction to Energy=                     0.248723
Thermal correction to Enthalpy=                   0.249905
Thermal correction to Gibbs Free Energy=          0.146981
Sum of electronic and zero-point Energies=           -2625.895249
Sum of electronic and thermal Energies=              -2625.864690
Sum of electronic and thermal Enthalpies=            -2625.863508
Sum of electronic and thermal Free Energies=         -2625.966432
-----------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2626.35937213     A.U. after   18 cycles
-----------------------------------------------------------------------
```

cis-1/5d

```
-----------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
```

```
Zero-point correction=                           0.218961 (Hartree/Particle)
Thermal correction to Energy=                    0.249244
Thermal correction to Enthalpy=                  0.250426
Thermal correction to Gibbs Free Energy=         0.148054
Sum of electronic and zero-point Energies=          -2625.891761
Sum of electronic and thermal Energies=             -2625.861478
Sum of electronic and thermal Enthalpies=           -2625.860296
Sum of electronic and thermal Free Energies=        -2625.962668
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2626.35731407     A.U. after   18 cycles
---------------------------------------------------------------------
```

5d⁺

```
---------------------------------------------------------------------
(SCRF)M06/BS1 (scrf=(solvent=1-butanol))
Temperature   373.150 Kelvin.  Pressure   1.00000 Atm.
Zero-point correction=                           0.218406 (Hartree/Particle)
Thermal correction to Energy=                    0.246588
Thermal correction to Enthalpy=                  0.247769
Thermal correction to Gibbs Free Energy=         0.151587
Sum of electronic and zero-point Energies=          -2165.527035
Sum of electronic and thermal Energies=             -2165.498853
Sum of electronic and thermal Enthalpies=           -2165.497671
Sum of electronic and thermal Free Energies=        -2165.593854
---------------------------------------------------------------------
(SCRF)M06+D3/BS2 (EmpiricalDispersion=GD3)
 SCF Done:  E(RM06) =  -2165.97877257     A.U. after   17 cycles
---------------------------------------------------------------------
```