Supramolecular Polymer and Sheet and a Double Cubane Structure in Platinum(IV) Iodide Chemistry: Solution of a Longstanding Puzzle

Mahmood A. Fard, Ava Behnia, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London N6A 5B7, Canada

Supporting Information

ABSTRACT: The complexes [PtMe₂(L)], L = 2-C₅H₄NCH₂NH-x-C₆H₄OH (x = 2, 3, or 4), react with iodine to form [PtI₂Me₂(L)], by trans oxidative addition, when x = 3 or 4, and they are shown to have polymeric or sheet structures formed through NH···I hydrogen bonding. However, ligand dissociation occurs when x = 2 to give [(PtI₂Me₂)ₙ] and, with methyl group transfer, the complex [(PtI₂Me₂·PtI₂Me₂)₂]. This tetraplatinum cluster complex is shown to have a double cubane structure, thus solving a longstanding puzzle.

INTRODUCTION

Trimethylplatinum iodide was the first alkyl complex of a transition metal to be reported, so it is important in the development of organometallic chemistry. Many related complexes have since been reported and they have the classic cubane structure [(PtXMe₃)₄], A, Chart 1, typically with X⁻ = halide, OH⁻, S R⁻, in which each platinum(IV) center is octahedral and each anion is triply bridging. There are also dialkylplatinum dihalides [(PtX₂R₂)ₙ], including those with R = Me and R₂ = C₃H₆ (the first metallacyclobutane complex), and mixed complexes [(PtXMe₃·PtX₂Me₂)ₙ]. On this basis of vibrational spectroscopy and mass spectrometry, as well as by analogy to the established structure A, the complexes [(PtXMe₃·PtX₂Me₂)ₙ] and [(PtX₂R₂)ₙ] were assigned cubane structures such as B or C, respectively, with two (B) or four (C) terminal Pt–X bonds as well as the four Pt₃(μ₃-X) groups. These halide complexes are insoluble in non-coordinating solvents, and it was not possible to grow crystals to confirm the proposed structures crystallographically. More recently, the complexes [(Pt(OH)Me₃·Pt(OH)₂Me₂)₂] and [(Pt(OH)Me₃·Pt(OMe)₂Me₂)₂] were prepared and shown to have the double cubane structure D, X = OH or OMe, which contain no terminal Pt–X bonds. It was suggested that the halide complexes [(PtXMe₃·PtX₂Me₂)ₙ] might also have this structure instead of B and that the complexes [(PtX₂R₂)ₙ] might have a polymeric structure E instead of C (Chart 1), but no proof was possible at that time. This paper describes the synthesis and structures of some new platinum(IV) iodide complexes and their supramolecular chemistry. In this study, crystals of the Hall cluster [(PtI₂Me₂·PtI₂Me₂)₂] were obtained, and it is finally proved after 47 years to have the double cubane structure D.

RESULTS AND DISCUSSION

As part of a study on the effect of ligands with hydrogen bonding substituents on reactivity and mechanism in oxidative addition reactions of dimethylplatinum(II) complexes, the aminopyridine ligands L₁–L₃, which contain phenol substituents at the amine donor, were studied (Scheme 1). The ligands contain both an NH group and an OH group, which might act as hydrogen bond donors. Ligand L₁ has been used often, but L₂ and L₃ are not so well-known and are incompletely characterized.

Received: June 18, 2018
Accepted: August 9, 2018
Published: August 30, 2018
[Pt₂Me₄(μ-SMe₂)₂], 1,12 and these ligands gave an equilibrium mixture, which contained cis-[PtMe₂(SMe₂)₂], 2,12, the expected product [PtMe₂(L)], 3−5, and free ligands L and SMe₂, as monitored by 1H NMR spectroscopy in acetone-d₆ solution (Scheme 1, Figures S5−S7), and they were not isolated but were prepared and used in solution for subsequent studies. As an example, in the 1H NMR spectrum for complex 3 in acetone-d₆, two methyl platinum resonances were observed at δ 0.24 and 0.65, with satellites with coupling constants 2J(PtH) = 86 and 90 Hz, respectively, in the range expected for methylplatinum(II) complexes.8 The complexes have no symmetry, and therefore, the CH₂ group has nonequivalent CHaHb protons.

The reactions of complexes 4 and 5 with iodine occurred in the expected way to give the corresponding platinum(IV) complexes 6 and 7 by trans oxidative addition (Scheme 2).13 The 1H NMR spectra of 6 contained two methylplatinum resonances at δ = 1.75, 2J(PtH) = 74 Hz, and δ = 2.40, 2J(PtH) = 75 Hz, and the lower values of the coupling constants indicate the formation of a platinum(IV) complex.8,13 The methylene group gave two sharp CHH₈ doublets of doublet peaks at δ(1H) = 5.08 [2J(H'H') = 15 Hz; 2J(CH₂−NH) = 4 Hz] and 5.53 [2J(H'H') = 15 Hz; 2J(CH₂−NH) = 12 Hz] (Figure S8). The NMR data are consistent with the proposed structure (Scheme 2) but do not define the stereochemistry. However, the structures were finally proved by structure determinations (Figure 1). Each platinum center contains two cis methyl groups, the chelate ligand L₃ or L₄, and two trans iodide ligands, as expected for the trans oxidative addition reaction. Complex 6 is not solvated, but the lattice of complex 7 contains an acetone solvate molecule, which is hydrogen-bonded to the phenol proton (Figure 1).

The reaction of the equilibrium mixture of complexes 2 and 3 in acetonitrile solution occurred in a different way to give [[PtMe₂PtI₂Me₂]₄], 8, and [[PtI₂Me₂]₅], 9, as shown in Scheme 3, with loss of the ligand L₁. The reaction immediately gave an insoluble brown precipitate, identified as mostly the known complex 9.4 Filtration of the mixture, followed by slow diffusion of ether into the acetonitrile solution, then gave orange crystals identified as complex 8.6 The formation of 8 requires a methyl-transfer reaction to form the trimethylplatinum(IV) groups and should also give a
monomethylplatinum complex which was not identified. Such methyl-transfer reactions are well-known and may occur either by direct methyl for halogen exchange or by a redox mechanism involving methyl iodide transfer from platinum(IV) to a dimethylplatinum(II) complex. The formation of 8 and 9 also requires dissociation of the ligands L1 and dimethylsulfide on the oxidation to platinum(IV), a reaction which is common with dimethylsulfide complexes but infrequent with chelate ligands. Steric effects of the ortho hydroxyl group in L1 probably account for the difference in the reaction of complex 3 with iodine compared to the simple oxidative addition observed for 4 and 5 (Scheme 2). This steric effect is not important in forming the platinum(II) complex 3 and indeed may be helpful in forming a Pt–HO hydrogen bond in 3, but is expected to be more important in an octahedral platinum(IV) complex analogous to 6 or 7. The structure of complex 9 shown in Scheme 3 is tentative, but the structure of 8 was determined and is shown in Figure 4. It finally confirms the prediction that the complex [[PtMe3·PtI2Me2]2, 8], has the face-bridged double cubane framework with two vertices missing and not the originally proposed simple cubane structure B (Chart 1). Each platinum(IV) center has octahedral stereochemistry. The two trimethylplatinum(IV) groups [Me3Pt(1) and Me3Pt(1A)] are at either end of the cluster, and the two dimethylplatinum(IV) units [Me2Pt(2) and Me2Pt(2A)] are at the center. Two of the iodide groups are triply bridging, μ3-I [I(2) and I(2A)], and the other four are doubly bridging, μ2-I ligands [I(1), I(1a), I(3), I(3a)]. The triply bridging μ3-I ligands [I(2) and I(2A)] are trans to carbon, and the Pt–I distances fall in the range 2.812(1)–2.814(1) Å. However, the doubly bridging, μ2-I groups [I(1), I(1a), I(3), I(3a)] are trans to both carbon and iodine, and the distances Pt(1)–I(3) = 2.814(1) and Pt(1)–I(1) = 2.808(1) Å trans to methyl are longer than the distances Pt(2)–I(3) = 2.644(1) and Pt(2)–I(1) = 2.634(1) Å.

**CONCLUSIONS**

The aminomethylpyridine ligands L1–L3 do not coordinate strongly to the dimethylplatinum(II) center, as shown by the inability to completely displace the dimethylsulfide ligands from [PtMe2(SMe2)2] (Scheme 1). Qualitatively, the equilibrium constants for the formation of the new

Figure 2. Supramolecular polymeric structure of complex 7. Intermolecular distances: N(2)···I(2B) = I(2)···N(2A) = 3.66(1) Å. Symmetry-related atoms: x, y, z; x, 1/2 − y, −1/2 + z; x, 3/2 − y, 1/2 + z.

Figure 3. Supramolecular sheet structure of complex 6. Intermolecular distances: N(2)···I(1A) = I(1)···N(2C) = 3.67(1); O(1)···I(2B) = I(2)···O(1D) = 3.58(1) Å. Symmetry-related atoms: x, y, z; −1/2 + x, y, 1/2 − z (A); −1/2 + x, 1/2 − y, −z (B); 1/2 + x, y, 1/2 − z (C); 1/2 + x, 1/2 − y, −z (D).

Scheme 3. Synthesis of Complexes 8 and 9

![Scheme 3](image-url)
dimethylplatinum(II) complexes follow the sequence $L_3 > L_1 > L_2$ (Scheme 2 and Figures S5–S7). However, $L_2$ and $L_3$ bind relatively more strongly to platinum(IV), compared to $L_1$, and selectively form $[\text{Pt}(\text{Me}_2\text{I})_2]$ by trans oxidative addition of iodine. These complexes form a supramolecular polymer ($L_3$) or sheet ($L_2$) by intermolecular hydrogen bonding. The ligand $L_1$ evidently binds less strongly and the complex $[\text{PtMe}_2(L_1)]$ reacts with iodide with loss of the ligand to form the bridging iodide complexes $[\text{PtMe}_2(\text{PtMe}_2\text{I})_2]$, $8$, and $[[\text{PtMe}_2\text{I}]]_2$.

Experimental Section

NMR spectra were recorded using Bruker 400, Inova 400, and Inova 600 NMR spectrometers. Spectra are referenced to tetramethylsilane and assignments are given according to the labeling scheme in Chart 2. Single-crystal X-ray diffraction

| Chart 2. NMR Labeling Scheme |
|---|
| ![Chart 2. NMR Labeling Scheme](image) |

measurements were made using a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Single crystals of the complexes were immersed in paraffin oil and mounted on MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL. Crystallographic data are given in the CIF files (CCDC 1834513–1834515). The ligand $L_1$ and complex $[\text{Pt}_2\text{Me}_4(\mu-S\text{Me}_2)]_2$ were synthesized according to literature procedures.

2-C$_3$H$_6$NCH$_2$NH-3-C$_6$H$_4$OH, L2. A solution of 3-amino-phenol (2.20 g, 20.20 mmol), 2-chloromethylpyridine hydrochloride (3.31 g, 20.20 mmol), and triethylamine (5.60 mL, 40.44 mmol) in ethanol (150 mL) was heated under reflux in ethanol for 8 h. The solvent was evaporated, the residue was dissolved in CH$_3$Cl$_2$ (100 mL), the solution was washed with water to remove salts, and then the solvent was evaporated. The product was purified by chromatography on a silica gel using ethyl acetate as the eluent. The first yellow fraction from the silica gel column was collected, the solvent was evaporated, and then yellow powder was dried in vacuo. Yield: 2.83 g, 70%. NMR in CD$_3$OD (400 MHz, 25 °C): $\delta(\text{H})$ 8.50 (d, 1H, J(HH) = 5 H$_6$, H$_6^\alpha$), 7.77 (dd, 1H, J(HH) = 9, 8 Hz, H$_8^\alpha$), 7.48 (d, 1H, J(HH) = 8 H$_6$, H$_6^\alpha$), 7.29 (dd, 1H, J(HH) = 5, 8 Hz, H$_8^\beta$), 6.90 (dd, 1H, J(HH) = 8, 9 Hz, H$_8$), 6.14 (1H, J(HH) = 8 H$_8$, H$_6$), 6.10 (1H, J(HH) = 8 H$_8$, H$_6$), 6.06 (s, 1H, H$_6$), 4.41 (s, 2H, CH$_2$); $\delta$(C) 161.6, 159.4, 151.2, 149.7, 138.9, 130.9, 123.6, 123.1, 106.2, 105.6, 100.9, 50.1 (CH$_2$).

2-C$_3$H$_6$NCH$_2$NH-4-C$_6$H$_4$OH, L3. A mixture of 4-aminophenol (4.00 g, 36.65 mmol) and 2-pyridinecarboxaldehyde (3.5 mL, 36.65 mmol) in tetrahydrofuran (60 mL) was stirred for 8 h. Solid NaBH$_4$ (1.85 g, 49 mmol) was added to the resulting mixture in portions. The solvent was evaporated, the residue was dissolved in CH$_3$Cl$_2$ (100 mL), the solution was washed with water to remove salts and dried over MgSO$_4$, and then the solvent was evaporated to give the product as a yellow powder. Yield: 5.36 g, 73%. NMR in CD$_3$OD (400 MHz, 25 °C): $\delta(\text{H})$ 8.46 (d, 1H, J(HH) = 5 H$_6$, H$_6^\alpha$), 7.72 (dd, 1H, J(HH) = 9, 8 Hz, H$_8^\alpha$), 7.45 (d, 1H, J(HH) = 8 H$_8$, H$_6$), 7.25 (dd, 1H, J(HH) = 5, 9 Hz, H$_8^\beta$), 6.60 (1H, J(HH) = 8 H$_8$, H$_6$), 5.61 (1H, J(HH) = 8 H$_8$, H$_6$). 4.35 (s, 2H, CH$_2$); $\delta$(C) 161.5, 150.5, 149.6, 142.8, 138.8, 123.6, 123.4, 117.0, 115.9, 51.3 (CH$_2$).

Formation of $[\text{PtMe}_2(L_1)]$. A solution of ligand $L_1$ (0.040 g, 0.200 mmol) in acetone (5 mL) was added a solution of ligand L1 (0.040 g, 0.200 mmol) in acetone (5 mL). The solution was stirred for 2 h under inert atmosphere, and the solvent was evaporated under vacuum to give the product in equilibrium with $[\text{PtMe}_2(\text{SMe}_2)]_2$ and free ligand. NMR in acetone-$d_6$: $\delta(\text{H})$ 8.82 (d, 1H, J(HH) = 5 H$_6$, H$_6^\alpha$), 8.08 (t, 1H, J(HH) = 8, 8 Hz, H$_8^\beta$), 7.59 (d, 1H, J(HH) = 8 H$_6$, H$_6^\alpha$), 7.45 (dd, 1H, J(HH) = 5, 8 Hz, H$_8^\alpha$), 7.21 (d, 1H, J(HH) = 8 H$_8$, H$_6$), 7.06 (dd, 1H, J(HH) = 7, 8 Hz, H$_8$), 6.89 (1H, J(HH) = 7, 8 Hz, H$_8$), 6.42 (1H, J(HH) = 8, 7 Hz, H$_8$), 6.60 (1H, J(HH) = 8 H$_8$, H$_6$), 4.65 (1H, J(HH) = 16 Hz, J(HH) = 5 Hz, H$_8$), 0.34 (s, 3H, J(PtH) = 8 Hz, Me$_3$).

Complexes 4 and 5 were prepared similarly. NMR in acetone-$d_6$: 4, $\delta(\text{H})$ 8.76 (d, 1H, J(HH) = 5 Hz, H$_6^\alpha$), 8.08 (dd, 1H, J(HH) = 9, 8 Hz, H$_8^\alpha$), 7.62 (1H, J(HH) = 8 Hz, H$_8^\alpha$), 7.38 (dd, 1H, J(HH) = 5, 9 Hz, H$_8^\beta$), 6.99 (t, 1H, J(HH) = 8 Hz, H$_8$), 6.65 (br, 1H, NH), 4.65 (1H, J(HH) = 16 Hz, J(HH) = 5 Hz, H$_8$), 4.34 (d, 1H, J(HH) = 16 Hz, J(HH) = 9 Hz, H$_8$), 0.65 (s, 3H, J(PtH) = 90 Hz, Me$_3$).

The solution was stirred for 6 h. The mixture was filtered, and
the filtrate was layered with pentane to give orange plate crystals after 2 days, which were collected, washed with pentane, and dried in vacuo. Yield: 0.09 g, 70%. Anal. Calcd for C18H18I2N2OPt: C, 27.69; H, 3.28; N, 3.80. Found: C, 28.03; H, 3.15; N, 3.80%. NMR in acetone-d6: δ(H) 8.74 (d, 1H, 3J(HH) = 6 Hz, H6), 8.07 (t, 1H, 3J(HH) = 9 Hz, H8), 7.3 (d, 1H, 3J(HH) = 8 Hz, H4), 7.65 (dd, 1H, 3J(HH) = 7, 8 Hz, H3), 7.4 (d, 2H, 3J(HH) = 9 Hz, H2), 6.88 (d, 2H, 3J(HH) = 9 Hz, H5), 6.4 (br, 1H, NH), 5.48 (d, 1H, 3J(HH) = 15 Hz, 3J(CH-NH) = 12 Hz, H7), 5.05 (d, 3J(HH) = 15 Hz, 3J(CH-NH) = 4 Hz, H8), 2.35 (s, 3J(PH) = 74 Hz, Me3), 1.73 (s, 3J(PH) = 73 Hz, Me3); δ(13C) 160.2, 155.9, 148.4, 140.4, 136.5, 126.0, 124.2, 121.1, 116.2, 61.2 (CH2), -14.3 (Me), -17.3 (Me).

[PtMe2L3]2+. To a stirred solution of [PtMe2(μ-SMe)2] (0.022 g, 0.039 mmol) in MeCN (5 mL) was added a solution of ligand L1 (0.015 g, 0.077 mmol) in MeCN (10 mL), followed by the addition of I2 (0.029 g). The mixture was stirred for 5 h to give a brown suspension. The mixture was filtered to remove [PtMe2I2]9− and the filtrate was layered with diethyl ether (50 mL). After 2 weeks, the orange block crystals of 8 which formed were collected, washed with pentane, and dried in vacuo. Yield: 0.013 g, 10%. Once formed, the crystals of 8 were insoluble in common organic solvents.4

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01367.

Selected NMR spectra and summary of crystallographic data (PDF)
Accession Codes: CCDC 1834513–1834515 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (CIF)

■ AUTHOR INFORMATION

Corresponding Author
E-mail: pudd@uw.ca (R.J.P.)

ORCID
Richard J. Puddephatt: 0000-0002-9846-3075

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the NSERC (Canada) for financial support.

■ REFERENCES

1. Pope, W. J.; Peachey, S. J. The alkyl compounds of platinum. J. Chem. Soc., Trans. 1909, 95, 571–576.
2. (a) Rundle, R. E.; Sturdivant, J. H. The crystal structures of trimethylplatinum chloride and tetramethylplatinum. J. Am. Chem. Soc. 1947, 69, 1561–1567. (b) Hoff, G. R.; Brubaker, C. H. Inorg. Chem. 1968, 7, 1655–1656.
3. (a) Hartley, F. R. The Chemistry of Platinum and Palladium; Applied Science: London, 1973. (b) Jain, V. K.; Rao, G. S.; Jain, L. The organic chemistry of platinum(IV). Adv. Organomet. Chem. 1987, 27, 113–168.
4. (a) Hall, J. R.; Swile, G. A. Preparation of some dimethylplatinum(IV) complexes. Aust. J. Chem. 1971, 24, 423–426. (b) Hall, J. R.; Swile, G. A. Dimethylplatinum(IV) compounds. II. Spectra and reactions of the compounds [Pt(CH3)2X2] (X = I, Br and Cl). J. Organomet. Chem. 1973, 56, 419–433. (c) Appleton, T. G.; D’Alton, C. J.; Hall, J. R.; Mathieson, M. T.; Williams, M. A. Synthesis of dimethylplatinum(IV) Compounds, [(PtMe2X)2], [(PtMe2XY)2], and, in solution, fac-[PtMe2X(H2O)2]4+, where X and Y are anionic ligands. Can. J. Chem. 1996, 74, 2008–2017.
5. Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; PIlbrook, M. F. Nature of Tipper’s compound dichlorotrimethylplatinum(IV) tetramer. J. Chem. Soc. A 1969, 1227–1231.
6. (a) Lawrence, C. D.; Tipper, C. F. H. Some reactions of cyclopropane, and a comparison with the lower olefins. 2. Some platinum-cyclopropane complexes. J. Chem. Soc. 1955, 2045–2046.
(b) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. Structure of cyclopropane platinum chloride. J. Chem. Soc. 1961, 738–742.
7. (a) Jennings, P. W.; Johnson, L. L. Metallacyclobutane complexes of the group 8 transition metals. Synthesis, characterization and chemistry. Chem. Rev. 1994, 94, 2241–2290. (d) Puddephatt, R. J. Platinacyclobutane chemistry. Coord. Chem. Rev. 1980, 33, 149–194.
8. (a) Safe, M. J.; Jennings, M. C. P.; Puddephatt, R. J. The chemistry of [PtMe2(1,2-bis(2-pyridyl)ethane): remarkable impact of an easily dissociated chelate ligand. Organometallics 2011, 30, 5625–5635. (b) Safe, M. S.; Jennings, M. C.; Puddephatt, R. J. A double cubane structure in organoplatinum(IV) chemistry. Chem. Commun. 2009, 1487–1489.
9. (a) Fard, M. A.; Behnia, A.; Puddephatt, R. J. Activation of dioxygen by dimethylplatinum(II) complexes. Organometallics 2017, 36, 4169–4178. (b) Thompson, K. A.; Kadwell, C.; Boyle, P. D.; Puddephatt, R. J. Reactivity of organoplatinum complexes containing appended alcohol functional groups: activation of dioxygen and hydrogen peroxide. J. Organomet. Chem. 2017, 829, 22–30.
(c) Moustafo, M. E.; Boyle, P. D.; Puddephatt, R. J. A biomimetic phenol substituent effect on the reaction of a dimethylplatinum(II) complex with oxygen: proton coupled electron transfer and multiple proton relay. Chem. Commun. 2015, 51, 10334–10336.
10. (a) Wong, Y.-L.; Ma, J.-F.; Xue, F.; Mak, T. C. W.; Ng, D. K. P. Dioxygen(VI) complexes with N2O tridentate ligands. Synthesis and structure of the chloro and alkyl derivatives. Organometallics 1999, 18, 5075–5079. (b) Kanamori, K.; Kusajima, K.; Yachi, H.; Suzuki, H.; Miyashita, Y.; Okamoto, K.-I. Synthesis, X-ray structures, and solution properties of vanadium(VI) and (IV) complexes with N(2-hydroxyphenyl)-N(2-pyridyl)-methylamine. Bull. Chem. Soc. Jpn. 2007, 80, 324–328.
11. (a) Liggand L2: Maksimovska, J.; Feng, L.; Harms, K.; Yi, C.; Kissil, J.; Marmorstain, R.; Meggers, E. Targeting large kinase active site with rigid, bulky octahedral ruthenium complexes. J. Am. Chem. Soc. 2008, 130, 15764–15765.
(11) Ligand L3: Walker, G. N.; Klett, M. A. Synthesis of varied heterocyclic and substituted aryl alkyl secondary amines, related Schiff bases and amides. *J. Med. Chem.* 1966, 9, 624−630.

(12) (a) Scott, J. D.; Puddephatt, R. J. Ligand dissociation as a preliminary step in methyl for halogen exchange reactions of platinum(II) complexes. *Organometallics* 1983, 2, 1643−1648. (b) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. Platinum(II) complexes of dimethyl sulfide. *Inorg. Synth.* 1997, 32, 149−153.

(13) Nabavizadeh, S. M.; Amini, H.; Rashidi, M.; Pellarin, K. R.; McCready, M. S.; Cooper, B. F. T.; Puddephatt, R. J. The mechanism of oxidative addition of iodine to a dimethylplatinum(II) complex. *J. OrganoMet. Chem.* 2012, 713, 60−67.

(14) (a) Sberegaeva, A. V.; Liu, W.-G.; Nielsen, R. J.; Goddard, W. A., III; Vedernikov, A. N. Mechanistic study of the oxidation of a methyl platinum(II) complex with O2 in water: PtIIIMe-to-PtIVMe and PtIIIMe-to-PtIVMe2 reactivity. *J. Am. Chem. Soc.* 2014, 136, 4761−4768. (b) Prantner, J. D.; Kaminsky, W.; Goldberg, K. I. Methylplatinum(II) and molecular oxygen: Oxidation to methylplatinum(IV) in competition with methyl group transfer To form dimethylplatinum(IV). *Organometallics* 2014, 33, 3227−3230. (c) Aye, K.-T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. W. Alkyl halide transfer from palladium(IV) to platinum(II) and a study of reactivity, selectivity and mechanism in this and related reactions. *Organometallics* 1989, 8, 1518−1522. (d) Scott, J. D.; Puddephatt, R. J. Comparison of the reactivities toward oxidative addition of the dimethylplatinum(II) units in mononuclear and binuclear complexes with biso(diamine) ligands. *Organometallics* 1986, 5, 2522−2529. (e) Ling, S. S. M.; Payne, N. C.; Puddephatt, R. J. Methyl group transfer on halogen oxidation of binuclear methylplatinum complexes – the mechanism of reaction and structure of a bridged platinum(IV)-platinum(II) product. *Organometallics* 1985, 4, 1546−1540. (f) Puddephatt, R. J.; Thompson, P. J. Methyl transfer reactions between platinum(II) and platinum(IV) complexes and some apparent methyl for hydride exchange reactions. *J. Organomet. Chem.* 1979, 166, 251−259. (g) Puddephatt, R. J.; Thompson, P. J. Methyl for halogen exchange reactions between palladium(II), platinum(II), gold(I) and gold(III) complexes. *J. Chem. Soc., Dalton Trans.* 1975, 1810−1814.

(15) (a) Nemec, I.; Herchel, R.; Machata, M.; Trávníček, Z. Tetranuclear Ni(II) and Co(II) Schiff-base complexes with an M4O8 defective dicubane-like core: zero-field SMM behavior in the cobalt analogue. *New J. Chem.* 2017, 41, 11258−11267. (b) Nakajima, T.; Seto, K.; Scheurer, A.; Kure, B.; Kajiwara, T.; Tanase, T.; Mikuriya, M.; Sakiyama, H. Tetranuclear nickel and cobalt complexes with an incomplete double-cubane structure. Homo- and heterometallic complexes and their 1D coordination polymers. *Eur. J. Inorg. Chem.* 2014, 5021−5033.