

Electronic and steric impact of bis-NHC ligands on reactions of Pt₃S₂ cores in trinuclear complexes bearing bis-NHC ligands with different lengths of alkylene bridges

Natsuki Yabune, Hiroshi Nakajima and Takanori Nishioka*

Department of Chemistry, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan.

Supplementary Information

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1. Experimental procedures

General Procedures: All chemicals were purchased from Sigma-Aldrich, Nacalai Tesque and Wako Pure Chemical Industries. All reagents and solvents were used as received. *cis*-[Pt(bisNHC-C2)(SH)₂] (bisNHC-C2 = 1,1'-Dimethyl-3,3'-ethylene-4-diimidazolilydene) was prepared according to the reported procedures.¹ *cis*-[Pt(bisNHC-C2)Cl₂] was synthesised from the reaction of K₂[PtCl₄] and [(bisNHC-C2)H₂](PF₆)₂ in DMSO using a previously reported procedure.¹ ¹H and ¹³C NMR spectra were recorded on Bruker AVANCE 400 or 600 FT-NMR spectrometers. Chemical shifts (δ in ppm, coupling constants *J* in Hz) for ¹H and ¹³C NMR signals are expressed from SiMe₄ and referenced to residual solvent resonances. Elemental analyses were performed on a J-Science Lab JM-10 elemental analyser by the Analytical Research Centre at Osaka City University.

Synthesis of [Pt(bisNHC-C2)(NCMe)₂](PF₆)₂

A solution of AgPF₆ (1.04 g, 4.12 mmol) in MeCN (10 mL) was added to a solution of *cis*-[Pt(bisNHC-C2)Cl₂] (0.93 g, 2.04 mmol) in MeCN (30 mL) to give a colourless solution with a white solid of AgCl. After the mixture was stirred for 3.5 h, the white solid was removed by centrifugation three times to give a colorless solution. The solvent was removed under reduced pressure to afford a white residue. The residue was re-dissolved in MeCN (15 mL) and insoluble white solids were removed by filtration using a membrane filter. The solvent was removed under reduced pressure to give a crude product of *cis*-[Pt(bisNHC-C2)(NCMe)₂] as a white solid. Recrystallisation of the crude product twice from a solution in MeCN by the addition of Et₂O to give colourless microcrystals. Yield: 1.43 g, 93%. Anal. Calcd for [Pt(bisNHC-C2)(NCMe)₂](PF₆)₂ (C₁₄H₂₀F₁₂N₆P₂Pt): C, 22.20; H, 2.75; N, 11.10. Found: C, 22.02; H, 2.75; N, 10.09. ¹H NMR (CD₃CN, 400 MHz, 293 K): δ 7.19 (d, ³J_{H-H} = 2.1 Hz, 2H, im), 7.14 (d, ³J_{H-H} = 2.1 Hz, 2H, im), 5.11 (ddd, ²J_{H-H} = 19.7 Hz, ³J_{H-H} = 8.1 Hz, ³J_{H-H} = 4.6 Hz, 2H, N-CH₂), 4.48 (ddd, ²J_{H-H} = 19.7 Hz, ³J_{H-H} = 8.1 Hz, ³J_{H-H} = 4.6 Hz, 2H, N-CH₂), 3.82 (s, 6H, N-Me). ¹³C NMR (CD₃CN, 100 MHz, 293 K): δ 133 (2-im), 125.0 (¹⁹⁵Pt satellites, ³J_{C-Pt} = 38.7 Hz, 4- or 5-im), 124.3 (¹⁹⁵Pt satellites, ³J_{C-Pt} = 45.1

Hz, 5- or 4-im), 123.0 (CD₃CN–Pt), 48.3 (¹⁹⁵Pt satellites, ³J_{C–Pt} = 16.9 Hz, N-CH₂), 38.7 (¹⁹⁵Pt satellites, ³J_{C–Pt} = 32.8 Hz, N-Me), 3.52 (septet, ¹J_{C–D} = 21.2 Hz, CD₃CN–Pt). The MeCN ligands were replaced with solvent molecules of CD₃CN.

Synthesis of [$\{\text{Pt}(\text{bisNHC-C2})\}_3(\mu_3\text{-S})_2\](\text{PF}_6)_2$

A mixture of *cis*-[Pt(bisNHC-C2)(SH)₂] (0.020 g, 0.045 mmol), *cis*-[Pt(bisNHC-C2)(NCMe)₂] (0.075 g, 0.099 mmol) and KHCO₃ (0.32 g, 3.2 mmol) as a proton scavenger in DMSO (10 mL) was stirred for 15 min to give a yellow mixture, which was heated at 60 °C for 2 h to afford a pale-yellow mixture. The solvent was removed under reduced pressure to give a pale-yellow solid. The solid was re-dissolved in water and added a solution of NH₄PF₆ (0.17 g 1.0 mmol) in water (5 mL) to give a white solid, which was collected by suction filtration and washed with water. The crude product was recrystallised from an solution in MeCN by diffusion of Et₂O. Yield: 0.058 g, 85%.
Anal. Calcd for [$\{\text{Pt}(\text{bisNHC-C2})\}_3(\mu_3\text{-S})_2\](\text{PF}_6)_2 \cdot \text{Et}_2\text{O}$ (C₃₄H₅₂F₁₂N₁₂OP₂Pt₃S₂): C, 25.78; H, 3.31; N, 10.61.
Found: C, 25.48; H, 3.15; N, 10.72. ¹H NMR (CD₃CN, 600 MHz, 298 K): C_s isomer: δ 7.04 (dd, ³J_{H–H} = 2.0, 2.1 Hz, 4H, im), 7.02–7.01 (m, 4H, im), 6.98 (d, ³J_{H–H} = 2.0 Hz, 2H, im), 6.93 (d, ³J_{H–H} = 2.0 Hz, 2H, im), 5.51–5.34 (m, 6H, N-CH₂), 4.37–4.30 (m, 6H, N-CH₂), 3.93 (s, 6H, N-Me), 3.90 (s, 6H, N-Me), 3.65 (s, 6H, N-Me). C_{3h} isomer: δ 7.02 (d, ³J_{H–H} = 2.0 Hz, 6H, 4-im), 6.95 (d, ³J_{H–H} = 2.0 Hz, 6H, 5-im), 5.51–5.34 (m, 6H, N-CH₂), 4.37–4.30 (m, 6H, N-CH₂), 3.73 (s, 18H, Me). ¹³C NMR (CD₃CN, 150 MHz, 298 K): C_s isomer: δ 159.0, 158.5, 156.4 (2-Im), 123.1, 122.7, 122.52, 122.47, 122.3, 122.04 (s, 4-Im, 5-Im), 48.99, 48.7, 48.4 (s, N-CH₂), 39.06, 39.04, 37.9 (s, N-Me). C_{3h} isomer: δ 158.1 (2-Im), 122.8 (s, 4-Im), 121.99 (s, 5-Im), 48.5 (s, N-CH₂), 38.3 (s, N-Me).

Synthesis of [$\text{Ag}\{\text{Pt}(\text{bisNHC-C2})\}_3(\mu_3\text{-S})_2\](\text{PF}_6)_5$

A solution of AgPF₆ (0.0066 g, 0.026 mmol) in MeCN (2 mL) was added to a solution of [$\{\text{Pt}(\text{bisNHC-C2})\}_3(\mu_3\text{-S})_2\](\text{PF}_6)_2$ (0.056 g, 0.037 mmol) in MeCN (3 mL). The solution was stirred for 15 min to give a yellow solution.

Diethyl ether (15 mL) was added to the solution to afford a yellow solid, which was collected by suction filtration and washed with diethyl ether. Yield: 0.022 g, 36%. Single crystals suitable for X-ray crystallography were obtained from a solution of a crude product in a mixed solvent of MeCN and MeOH by diffusion of Et₂O. Anal. Calcd for C₆₀H₈₄AgF₃₀N₂₄P₅Pt₆S₄: C, 22.02; H, 2.59; N, 10.27. Found: C, 22.09; H, 2.84; N, 10.48.

2. X-ray crystallography

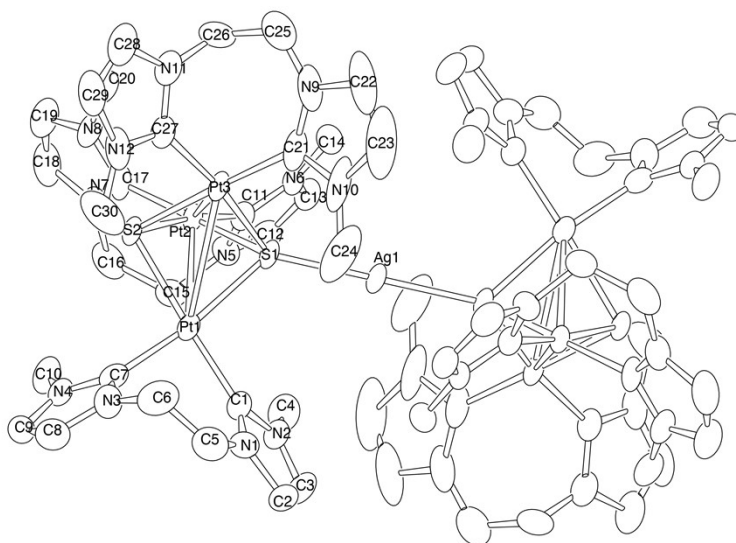


Fig. S-1 Atom numbering for [4]⁵⁺

A single crystal of [4](PF₆)₆•2MeOH was mounted on a loop using Paratone. Diffraction data were collected on a Rigaku Varimax Saturn724 diffractometer using a rotation method with 0.5° frame widths. The data were integrated, scaled, sorted, and averaged using the CrystalClear² software. Absorption corrections were applied using the multi-scan method. The structures were solved using SHELXS97³ and refined with SHELXL Version 2018/3⁴ using the CrystalStructure software.⁵ All hydrogen atoms were located at the calculated positions and refined as riding models. Crystallographic data are summarised in Table S1.

Table S1. Crystallographic data of triplatinum complex [4](PF₆)₅•2MeOH.

| | |
|---|--|
| Formula | C ₆₂ H ₉₂ AgF ₃₀ N ₂₄ O ₂ P ₅ Pt ₆ S ₄ |
| <i>M_w</i> | 3337.04 |
| Crystal description | colourless, prism |
| Crystal size/mm | 0.120 × 0.097 × 0.039 |
| Crystal system | <i>triclinic</i> |
| Space group | <i>P</i> $\bar{1}$ (#15) |
| <i>a</i> /Å | 13.456(3) |
| <i>b</i> /Å | 14.916(3) |
| <i>c</i> /Å | 15.624(3) |
| α /° | 66.163(11) |
| β /° | 71.936(14) |
| γ /° | 73.777(14) |
| <i>V</i> /Å ³ | 2683.8(10) |
| <i>Z</i> | 1 |
| <i>F</i> (000) | 1572.00 |
| ρ_{calcd} /g cm ⁻³ | 2.065 |
| μ /mm ⁻¹ | 8.1874 |
| Total reflections | 21981 |
| Unique reflections (<i>R</i> _{int}) | 11830 (0.0358) |
| Scan range θ /° | 27.475 |
| Completeness | 0.957 |
| Index ranges | -14 ≤ <i>h</i> ≤ 17 -19 ≤ <i>k</i> ≤ 16 -20 ≤ <i>l</i> ≤ 20 |
| Data/restraints/para. | 11830/0/595 |
| <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)], <i>wR</i> 2 (all data) | 0.0580, 0.1609 |
| GOF on <i>F</i> ² | 1.010 |
| Max./min. ρ /eÅ ⁻³ | 2.50/-3.28 |
| Min./max. <i>T</i> | 0.550/0.727 |

Table S2. Selected bond distances for [4](PF₆)₅•2MeOH.

| Atoms | Distance/Å | Atoms | Distance/Å |
|---------|------------|---------|------------|
| Pt1–Pt2 | 3.1960(9) | Pt1–Pt3 | 3.1808(9) |
| Pt2–Pt3 | 3.2327(9) | Ag1–S1 | 2.349(2) |
| Pt1–S1 | 2.385(3) | Pt1–S2 | 2.368(3) |
| Pt2–S1 | 2.371(3) | Pt2–S2 | 2.364(3) |
| Pt3–S1 | 2.377(2) | Pt3–S2 | 2.364(2) |
| Pt1–C1 | 1.993(13) | Pt1–C7 | 1.976(11) |
| Pt2–C11 | 1.979(11) | Pt2–C17 | 2.007(12) |
| Pt3–C21 | 2.029(12) | Pt3–C27 | 1.999(10) |

Table S3. Selected bond angles for [4](PF₆)₅•2MeOH.

| Atoms | Angle/° | Atoms | Angle/° |
|-------------|------------|-------------|------------|
| Pt2–Pt1–Pt3 | 60.92(2) | Pt1–Pt2–Pt3 | 59.31(2) |
| Pt1–Pt3–Pt2 | 59.771(19) | | |
| Pt1–S1–Ag1 | 126.26(13) | Pt2–S1–Ag1 | 128.74(13) |
| Pt3–S1–Ag1 | 131.64(10) | S1–Ag1–S1* | 180.00(14) |
| S1–Pt1–S2 | 77.30(9) | S1–Pt1–C1 | 100.7(3) |
| S1–Pt1–C7 | 171.9(4) | S2–Pt1–C1 | 177.4(3) |
| S2–Pt1–C7 | 94.6(4) | C1–Pt1–C7 | 87.3(5) |
| S1–Pt2–S2 | 77.65(9) | S1–Pt2–C11 | 101.4(3) |
| S1–Pt2–C17 | 171.5(3) | S2–Pt2–C11 | 174.1(3) |
| S2–Pt2–C7 | 94.5(3) | C11–Pt2–C17 | 86.7(5) |
| S1–Pt3–S2 | 77.53(8) | S1–Pt3–C21 | 100.8(3) |
| S1–Pt3–C27 | 170.1(3) | S2–Pt3–C21 | 178.2(4) |
| S2–Pt3–C27 | 92.7(3) | C21–Pt3–C27 | 89.0(4) |
| Pt1–S1–Pt2 | 84.43(7) | Pt1–S1–Pt3 | 83.81(8) |
| Pt2–S1–Pt3 | 85.81(8) | Pt1–S2–Pt2 | 84.99(7) |
| Pt1–S2–Pt3 | 84.48(9) | Pt2–S2–Pt3 | 86.28(8) |

* Symmetry operation: 2–x, 1–y, –z

3. ¹H NMR spectrum at 253 K and mass spectrum of [2](PF₆)₂ in the presence of 1 eq. Ag(PF₆).

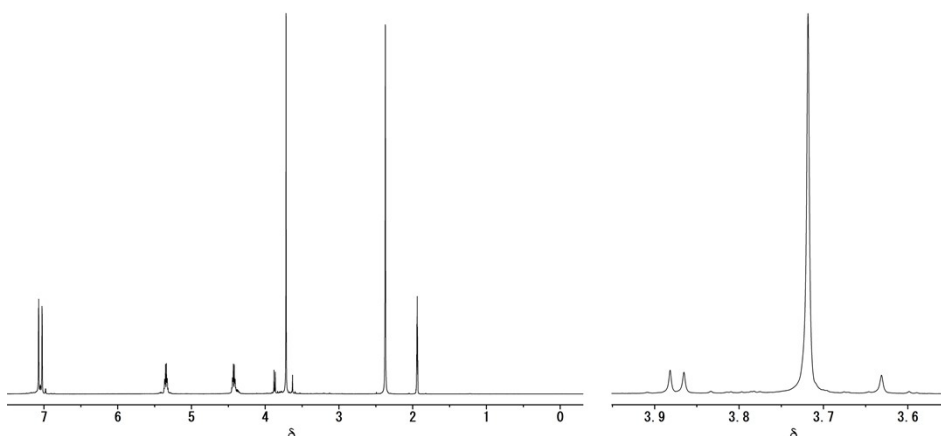


Fig. S-2 ¹H NMR spectrum at 253 K of [2](PF₆)₂ in the presence of 1 eq. Ag(PF₆).

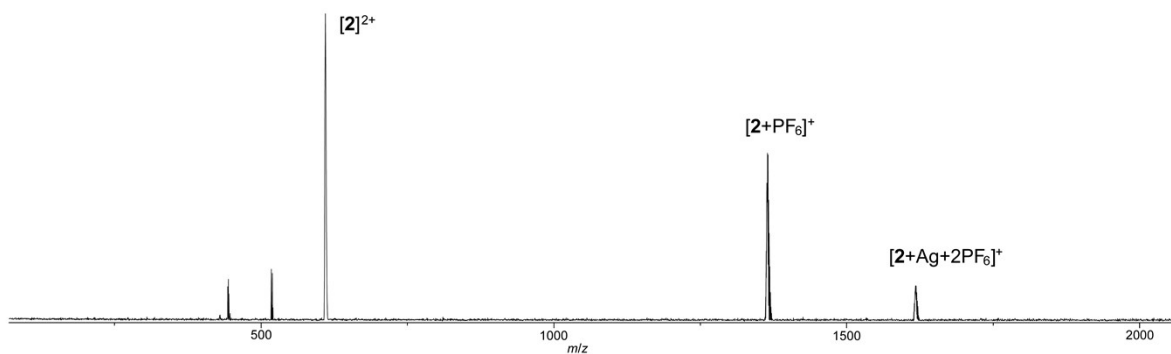


Fig. S-3 ESI-mass spectrum of $[2](PF_6)_2$ in the presence of 1 eq. $Ag(PF_6)$.

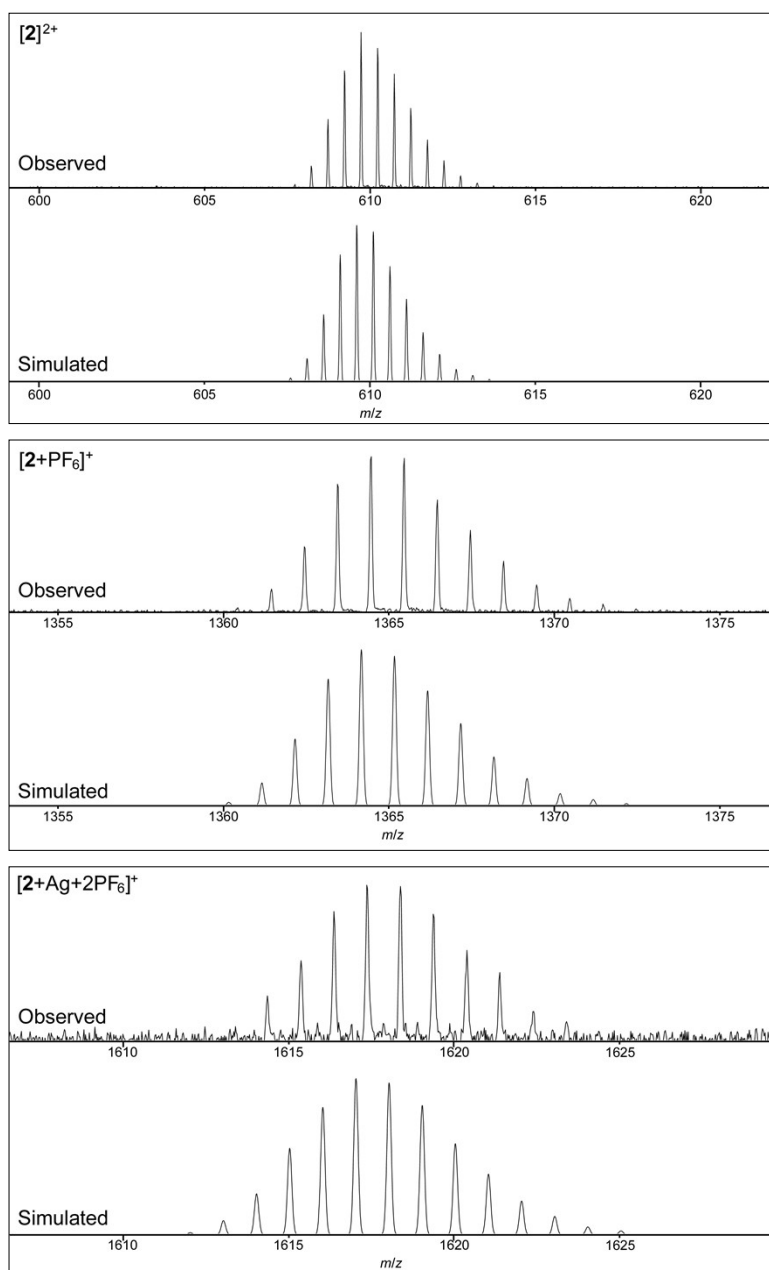


Fig. S-4 Expanded ESI-mass signals and their simulated ones of $[2](PF_6)_2$ in the presence of 1 eq. $Ag(PF_6)$.

4. References

- 1 Y. Maeda, H. Hashimoto and T. Nishioka, *Chem. Lett.*, 2012, **41**, 145-147; Y. Maeda, H. Hashimoto and T. Nishioka, *Dalton Trans.*, 2012, **41**, 12038-12047.
- 2 *CrystalClear*, Rigaku Corporation, 1999; *CrystalClear Software User's Guide*, Molecular Structure Corporation, 2000; J. W. Pflugrath, *Acta Cryst.*, 1999, **D55**, 1718–1725.
- 3 *SHELXL97*: G. M. Sheldrick, *Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.
- 4 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.
- 5 *CrystalStructure 4.3*: Crystal Structure Analysis Package, Rigaku Corporation (2000–2019), Tokyo 196-8666, Japan.