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Notes

C−S Bond Cleavage by Chloride in a Thioether N_2S_2 Complex of Platinum

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Introduction

Recent work has shown that it is possible to induce acidity in derivatized thioether $-CH_2$ moieties by coordination of transition metal ions.[1] Such reactions may lead to cyclometalation,[2] rearrangement[3] or C−S bond cleavage.[4] These reactions have implications for a variety of fields in chemistry such as organic synthesis,[5] biological chemistry,[6] and HDS processes.[7] The focus of C−S bond cleavage reactions in many systems has been S-alkylation/S-dealkylation reactions.[8] However in systems with flexible ligands C−S bond cleavage and rearrangement are frequently associated. This often causes the formation of anionic ligands, which are retained in the coordination sphere of the activating metal.[1,3] Here we report the rearrangement of a monomeric Pt complex leading to C−S bond cleavage and formation of an unusual dimer containing both thiolate and thioether donors.

Experimental Section

Reactions were carried out under a N_2 atmosphere. Solvents were distilled over standard drying reagents. Precursors were prepared by literature procedures.[9−11] NMR spectra were recorded on a Varian 300- or 200-MHz spectrometer. ^{195}Pt NMR spectra were recorded on the former operating at 64.50 MHz and referenced to $[PtCl_6]^{2-}$ [δ(^{195}Pt) 0]. Molar mass determinations were performed with a Hitachi Perkin-Elmer molecular weight apparatus (model 115). Elemental analyses were performed in the Campbell Microanalytical Laboratory at the University of Otago.

1,3-Bis(((6′-methyl-2′-pyridyl)thiomethyl)methyl)benzene (L1). A solution of 2-(chloromethyl)-6-methylpyridine (3.08 g, 21.8 mmol) and 1,3-bis(thiomethyl)benzene (1.85 g, 10.7 mmol) in 150 mL of CH_2Cl_2 was added to NaOH (4.50 g) in 80% ethanol (100 mL) and stirred for 24 h. The solvent was removed *in vacuo.* The resultant orange residue was taken up in CH_2Cl_2 (100 mL) and washed with Na_2CO_3 (3 × 70 mL) solution. The organic portion was dried ($MgSO_4$) and purified on a silica gel column eluted with CH_2Cl_2 to give a white crystalline solid. Yield: 50%, mp 74 °C. NMR (200 MHz, $CDCl_3$, δ, ppm): ^{1}H 7.45 (t, 2H, $^3J = 7.56$ Hz), 7.29−7.20 (m, 4H), 7.06 (d, 2H, $^3J = 7.50$ Hz), 6.95 (d, 2H, $^3J = 7.56$ Hz), 3.69 (s, 4H), 3.66 (s, 4H), 2.50 (s, 6H); ^{13}C{^{1}H} 157.8, 138.3, 136.7, 129.7, 128.5, 127.7, 121.3, 110.9, 37.5, 35.8, 24.4. ES-MS (1:1 CH_3CN/H_2O): *m/z* 381.3 (**L1**H^+). Anal. Calcd for $C_{22}H_{24}N_2S_2$: C, 69.43; H, 6.36; N, 7.36; S, 16.85. Found: C, 69.23; H, 6.54; N, 7.27; S, 16.80.

6-Methyl-2-(methylthiol)pyridine (L2+H). A suspension of 2-(chloromethyl)-6-methylpyridine (1.94 g, 0.0137 mol) and thiourea (1.04 g, 0.0137 mol) in ethanol (50 mL) was refluxed for 2 h, and solvent was removed *in vacuo*. The resulting residue was dissolved in H_2O (50 mL) and refluxed for 10 h with excess KOH (2 g). The reaction was neutralized with 9 M H_2SO_4 at 0 °C, extracted with CH_2Cl_2, dried ($MgSO_4$), and reduced *in vacuo* to give 1.74 g of brown oil. Yield: 91.2%. NMR (200 MHz, $CDCl_3$, δ, ppm): ^{1}H 7.53 (t, 1H, $^3J = 7.68$ Hz), 7.13 (d, 1H, $^3J = 7.62$ Hz), 7.01 (d, 1H, $^3J = 7.70$ Hz), 3.81 (2H, br) 2.54 (3H, s), 2.02 (1H, br); ^{13}C{^{1}H} 157.8, 155.9, 136.7, 121.6, 120.5, 44.4, 23.9. Anal. Calcd for C_7H_9NS: C, 60.39; H, 6.52; N, 10.06; S, 23.03. Found: C, 60.15; H, 6.21; N, 10.33; S, 22.79.

[Pt(L1)](PF_6)$_2$. Using a modified literature procedure,[12] the reaction of K_2PtCl_4 (100 mg, 0.241 mmol) and **L1** (91.7 mg, 0.241 mmol) in refluxing H_2O/MeOH (2:3 v/v, 50 mL) for 3 h gave a pale yellow solution. Addition of excess NH_4PF_6 gave a white solid that was washed with cold MeOH followed by cold diethyl ether and dried *in vacuo*. Yield: 85%. NMR (200 MHz, CD_3CN, δ, ppm): ^{1}H 8.27 (t, 2H, $^3J =$ 7.84 Hz), 7.98 (d, 2H, $^3J = 10.3$ Hz), 7.69−7.54 (m, 4H), 7.33 (d, 2H, $^3J = 7.98$ Hz), 4.83 (d, 2H, $^2J = 16.1$ Hz), 4.67 (d, 2H, $^2J = 16.1$ Hz), 3.90 (d, 2H, $^2J = 12.9$ Hz), 3.86 (d, 2H, $^2J = 12.9$ Hz), 2.42 (s, 6H); ^{13}C{^{1}H} 162.4, 157.8, 145.3, 133.8, 131.0, 130.7, 130.4, 127.8, 124.1, 45.7, 40.0, 25.1; ^{195}Pt −3484. FAB-MS*:* *m/z* 576.2 [^{195}Pt(**L1**)H$^+$]. $\Lambda = 227\ \Omega^{-1}\ cm^2\ mol^{-1}$, $M = 862$ g mol^{-1} Anal. Calcd for $C_{22}H_{24}N_2S_2$-PtP_2F_{12}: C, 30.52; H, 2.79; N, 3.24; S, 7.41, Cl 0.00. Found: C, 30.80; H, 2.79; N, 3.30; S, 7.65; Cl, 0.79.

[Pt$_2$(L1)(L2)Cl](PF_6)$_2$·2CH_3CN·H_2O. X-ray-quality cubic crystals were grown by slow evaporation and rearrangement of [Pt(**L1**)](PF_6)$_2$ in an acetonitrile/toluene solution. Data for the crystals. NMR (300 MHz, CD_3CN, δ, ppm): ^{1}H 8.44 (s, 1H, *meta*-H), 8.15 (t, 1H, $^3J =$ 7.80 Hz), 8.01 (t, 2H, $^3J = 7.80$ Hz), 7.84 (d, 1H, $^3J = 7.80$ Hz), 7.67 (t, 1H, $^3J = 7.50$ Hz), 7.53 (d, 2H, $^3J = 7.80$ Hz), 7.44 (d, 1H, $^3J =$ 7.50 Hz), 7.40 (d, 1H, $^3J = 7.50$ Hz), 7.19 (t, 1H, $^3J = 7.50$ Hz), 6.93 (t, 1H, $^3J = 8.40$ Hz), 5.26 (d, 1H, $^2J = 16.5$ Hz), 4.99 (d, 1H, $^2J =$ 16.5 Hz), 4.76 (d, 1H, $^2J = 16.8$ Hz), 4.74 (d, 1H, $^2J = 16.5$ Hz), 4.86−4.78 (m, 3H), 4.18 (d, 1H, $^2J = 14.4$ Hz), 3.65 (d, 1H, $^2J = 12.3$ Hz), 3.36 (d, 1H, $^2J = 12.3$ Hz), (CH_3 peaks obscured by peaks of

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Table 1. Crystal Data for $[Pt_2(\mathbf{L1})(\mathbf{L2})Cl](PF_6)_2 \cdot 2CH_3CN \cdot H_2O$

formula	$C_{33}H_{38}ClF_{12}N_5OP_2Pt_2S_3$	fw	1332.43
a, Å	11.3838(2)	space group	$P\bar{1}$ (No. 2)
b, Å	12.6850(3)	T, K	148(2)
c, Å	15.7144(3)	λ(Mo Kα), Å	0.710 73
α, deg	96.209(1)	d_{calc}, g cm^{-3}	2.098
β, deg	110.624(1)	μ(Mo Kα), cm^{-1}	0.700
γ, deg	90.382(1)	R$_1$[a]	0.0327
V, Å^3	2108.88(7)	wR$_2$[b]	0.0617
Z	2		

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Pt_2(\mathbf{L1})(\mathbf{L2})Cl](PF_6)_2 \cdot 2CH_3CN \cdot H_2O$

Pt(1)−N(3)	2.090(3)	Pt(2)−Cl(1)	2.3360(9)
Pt(1)−N(2)	2.095(3)	S(1)−C(7)	1.815(4)
Pt(1)−S(2)	2.2658(10)	S(1)−C(8)	1.846(4)
Pt(1)−S(3)	2.2910(9)	S(2)−C(16)	1.821(4)
Pt(2)−N(1)	2.089(3)	S(2)−C(15)	1.861(4)
Pt(2)−S(1)	2.2598(9)	S(3)−C(29)	1.843(4)
Pt(2)−S(3)	2.2818(9)		
N(3)−Pt(1)−N(2)	100.57(13)	S(1)−Pt(2)−Cl(1)	171.11(3)
N(3)−Pt(1)−S(2)	173.63(9)	S(3)−Pt(2)−Cl(1)	83.44(3)
N(2)−Pt(1)−S(2)	81.89(10)	C(7)−S(1)−Pt(2)	94.95(13)
N(3)−Pt(1)−S(3)	78.70(9)	C(8)−S(1)−Pt(2)	107.46(14)
N(2)−Pt(1)−S(3)	175.79(9)	C(16)−S(2)−Pt(1)	93.13(14)
S(2)−Pt(1)−S(3)	99.28(3)	C(15)−S(2)−Pt(1)	107.85(14)
N(1)−Pt(2)−S(1)	82.51(9)	C(29)−S(3)−Pt(2)	110.76(13)
N(1)−Pt(2)−S(3)	177.09(9)	C(29)−S(3)−Pt(1)	90.29(13)
S(1)−Pt(2)−S(3)	97.14(3)	Pt(2)−S(3)−Pt(1)	117.86(4)
N(1)−Pt(2)−Cl(1)	96.45(9)		

dissolved water); $^{13}C\{^1H\}$ 142.6, 142.5, 141.4, 135.2, 131.0, 130.8, 130.4, 128.7, 128.3, 127.6, 125.4, 123.4, 122.6, 49.5, 48.4, 43.7, 42.1, 41.2, 27.9, 26.2, 25.2; ^{195}Pt −3303, −3398. Anal. Calcd for $C_{29}H_{32}N_3S_3ClPt_2P_2F_{12}$; C, 28.22; H, 2.61; N, 3.40; S, 7.79. Found: C, 29.08; H, 2.72; N, 3.89; S, 7.52.

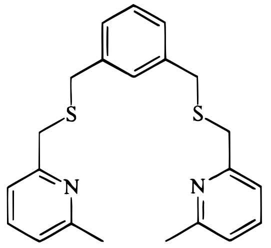
Bulk Preparation. K_2PtCl_4 (70 mg, 0.168 mmol), **L1** (32.1 mg, 0.084 mol), **L2** (11.8 mg, 0.084mol), and $NaOOCCH_3 \cdot 3H_2O$ (9.8 mg, 0.084 mol) in H_2O/MeOH (50 mL) were refluxed for 2 h to give a yellow suspension. After filtration, excess NH_4PF_6 was added to the filtrate to give a yellow powder, which was washed with cold MeOH and diethyl ether and dried *in vacuo*. Yield: 40%. Anal. Calcd for $C_{29}H_{32}N_3S_3ClPt_2P_2F_{12}$; C, 28.22; H, 2.61; N, 3.40; S, 7.79. Found: C, 28.40; H, 2.86; N, 3.22; S, 7.45.

X-ray Structure Determination. Crystals were initially grown by slow diffusion of diethyl ether into a CH_3CN solution. Data collected from one of these crystals yielded a structure that was identical to the one reported but of poorer quality. Suitable yellow cubes were finally obtained by slow evaporation from CH_3CN/toluene. These crystals have microanalyses consistent with the bulk material (vide supra). Crystallographic data are given in Table 1. A Siemens Smart-CCD system with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) was used to collect a hemisphere of intensity data in 1336 frames with increasing φ and a small amount with increasing ω to ensure complete coverage (width 0.3° per frame). Final cell constants were calculated from 8192 reflections from the data collection. A total of 9997 [$R_{int} = 0.0243$] unique data were corrected for Lorentz and polarization effects.[13] A multiscan absorption correction[14] was applied with $T_{min,max} = 0.653$, 1.000. No decay correction was necessary.

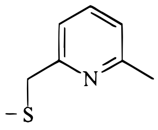
On the basis of systematic absences, E statistics, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The structure was solved with direct methods[15] and difference Fourier synthesis maps and was refined[16] with full-matrix least-squares techniques using 540 parameters. Non-hydrogen atoms were refined with anisotropic thermal parameters, and H atoms were placed in ideal positions and were refined as riding atoms with individual isotropic thermal parameters. Two CH_3CN molecules and a water molecule of solvation were found in the asymmetric unit. Two of three PF_6^- anions sit on special positions. Maximum residual electron density, possibly a Fourier ripple, of 1.67 e Å^{-3} was 0.97 Å from Pt(1). See Tables 1 and 2.

Results and Discussion

Synthesis and Characterization. Ligand **L1** was prepared by the base coupling of 2-(chloromethyl)-6-methylpyridine[10] and 1,3-bis(thiomethyl)benzene[11] in a 2:1 mole ratio. Purification by column chromatography gave a white air-stable crystalline solid. The parent thiol of **L2** was made via the isothiouronium salt and deprotonated by sodium acetate before use.



L1



L2

The stoichiometric reaction of **L1** and K_2PtCl_4 in refluxing H_2O/MeOH followed by the addition of excess NH_4PF_6 produced a white complex, in high yield, which analyzed as $[Pt(\mathbf{L1})](PF_6)_2$. The ^{1}H NMR spectra in CD_3CN and d_6-acetone showed four CH_2 doublets and a single methyl peak, the ^{13}C NMR spectra showed in total 12 peaks and a single peak was observed at −3484 ppm in the ^{195}Pt NMR spectrum. These data are consistent with a symmetrical structure. The compound was determined to be a monomer in acetone by molar mass determination using the vapor pressure (isopiestic) method.[17] Conductivity measurements indicated a 2:1 electrolyte in CH_3CN. The presence of the parent ion $[^{195}Pt(\mathbf{L1})H]^+$ at 576.2 *m/z* in the FAB mass spectrum and the ion $\{[^{195}Pt(\mathbf{L1})]PF_6\}^+$ at 720.0 *m/z* in the electrospray (ES) mass spectrum provided further conformation that the complex had the form $[Pt(\mathbf{L1})](PF_6)_2$.

Slow evaporation of a solution of $[Pt(\mathbf{L1})](PF_6)_2$ in CH_3CN/toluene produced yellow block crystals after about a week. The ^{1}H and COSY NMR spectra of these crystals displayed 10 CH_2 doublets and three methyl signals; the ^{13}C NMR spectrum displayed five CH_2 peaks and three CH_3 peaks showing a loss of symmetry and implying the presence of an additional $H_3C-C_5H_3N-CH_2-$ moiety. The ^{195}Pt NMR spectrum showed two signals at −3303 and −3398 ppm, shifted to higher frequency, indicating the presence of two Pt centers. Isolation of the dimer from two separate attempts to crystallize different samples of the monomer indicated the reproducible nature of the transformation.

X-ray Structure of $[Pt_2(L1)(L2)Cl](PF_6)_2 \cdot 2CH_3CN \cdot H_2O$. The two Pt atoms have pseudo-square-planar coordination. Each Pt atom is coordinated to an arm of **L1** in cis fashion through a pyridine and thioether group (Figure 1). The arms are folded such that each thioether group is on the same side of the ring

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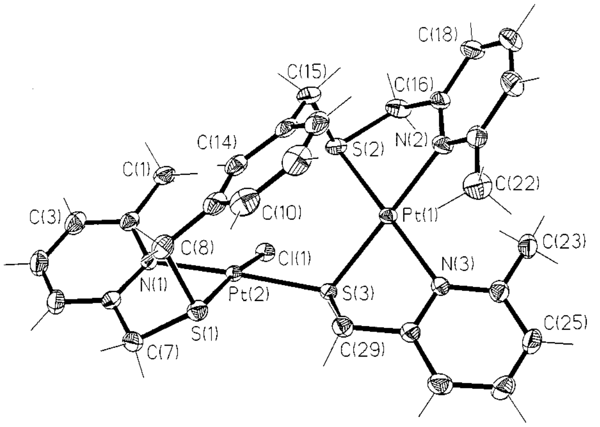


Figure 1. View of $[Pt_2(\mathbf{L1})(\mathbf{L2})Cl]^{2+}$ (crystallographic numbering). Thermal ellipsoids are drawn with boundary surfaces at the 50% level.

with respect to the linking *meta*-arene group. One arm twists forward of the *meta*-arene group while the other twists back and in both cases the pyridine nitrogen atoms point inward toward the *meta*-arene. The two Pt centers are linked by a bridging thiolate from the $H_3C-C_5H_3N-CH_2-S^-$, ligand **L2**. The thiolate is trans to both the pyridine donors of **L1**. Ligand **L2** appears to originate from C−S bond cleavage of **L1** (vide infra). Coordination of the pyridine group of **L2** completes the pseudo-square-planar arrangement about Pt(1). The pseudo-square-planar arrangement about Pt(2) is completed by the presence of a Cl^- ligand. The adventitious Cl^- originates from the starting material. The two $Pt-S_{thioether}$ bond lengths are very similar to values found for related Pt-thioether complexes.[18] The $Pt-S_{thiolate}$ bonds are slightly longer than the $Pt-S_{thioether}$ bonds but comparable to other reported values.[19] The Pt centers each lie in the plane of the donor atoms [average mean plane deviations Pt(1)−N(2)−S(2)−S(3)−N(3) 0.0793 Å; Pt(2)−N(1)−S(1)−S(3)−Cl(1) 0.0673 Å] and have very distorted bond angles. Bond angles about the Pt centers for *cis*-related ligands are in the range 78.70(9)−100.6(1)° for Pt(1) and 82.51(9)−97.14(3)° for Pt(2). The two pseudo-square planes are twisted by 72.2(1)° with respect to each other. The dimeric complexes form centrosymmetric-tetramer units in which the pseudo-square planes about Pt(2) sit in a staggered fashion over each other [Pt···Pt distance 3.811 Å]. The other pseudo-square plane twists away and is not involved in any interactions. The principal interactions forming the tetramer are $\pi-\pi$ interactions of the pyridine ring of the thiolate and the pyridine ring of **L2** attached to Pt(2) with their symmetry related counterparts [inter-ring distance 3.558 (9) Å]. There are a number of other weak attractive interactions involving the heavier elements [Pt(2)···S(3), 3.603 Å; Pt(2)···Cl(1), 3.900 Å; S(1)···Cl(1), 3.486 Å], which help to hold the complexes together (Figure 2).

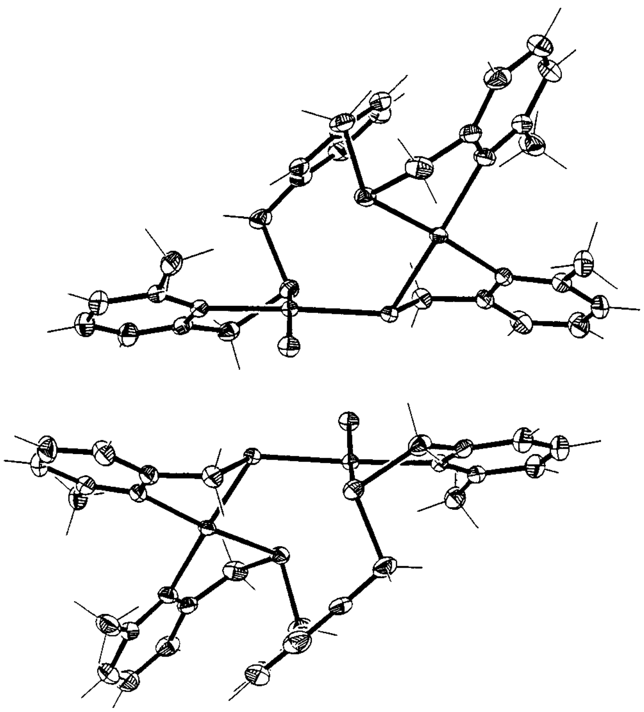
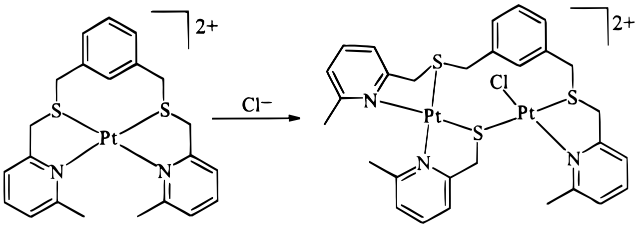


Figure 2. View of centrosymmetric tetrameric unit showing $\pi-\pi$ interactions and Pt(2)···Pt(2) arrangement.

The transformation of $[Pt(\mathbf{L1})]^{2+}$ during recrystallization to $[Pt_2(\mathbf{L1})(\mathbf{L2})Cl]^{2+}$ accounted for the observed changes in the NMR spectra. The Cl^- appeared to come from an impurity in the monomer. Repeat analyses showed the monomer contained between 0.8 and 1.7% residual Cl from K_2PtCl_4 starting material. The transformation was evident in the ^1H NMR spectra of the monomer, in CD_3CN and acetone-d_6. Upon removing solvent and redissolving the sample, peaks characteristic of the monomer decreased in intensity while those of the dimer began to appear. However the spectra also contained other peaks which may belong to intermediate species or other transformation products. Addition of Cl^- also caused the same changes. The FAB mass spectrum of the monomer gave a number of peaks which could be assigned to various fragmentation products confirming the fragility of the platinum bound C−S bond. The ES mass spectrum of the monomer also showed similar fragmentation products. However in contrast the ES mass spectrum of **L1** showed only a single intact, parent-ion peak. This suggests the cleavage of C−S bonds is enhanced by the presence of the electron-withdrawing Pt(II) center.[3]

Considering the experimental data, we propose the following transformation pathway. The transformation is initiated by nucleophilic attack of Cl^- on the α carbon of the arene of a monomer.[20] Attack causes C−S bond cleavage and results in thiolate formation (Scheme 1). This is supported by ^1H NMR experiments which show that the monomer remained unchanged in solution until addition of Cl^- or the solution was concentrated. The monomer showed no fluxional behavior in solution suggesting any unraveling of **L1** cannot occur before Cl^- attack.

Scheme 1



The newly formed thiolate attacks the Pt center of another monomer to form a bridging thiolate causing some unraveling

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of **L1**.[21] This partially unraveled ligand displaces the chlorinated byproduct and the presence of this byproduct can be identified in ES mass spectra. Finally acquisition of a Cl^- by the second Pt center completes dimer formation.

Interestingly, it was possible to assemble the dimer from its constituent parts. Reaction of **L1**, **L2**, and $PtCl_4^{2-}$ in refluxing methanol followed by treatment with excess PF_6^- gave the dimer as a yellow powder in 40% yield. The same product can thus be formed from both the decomposition of the monomer and the self-assembly of the constituent ligands. This indicates that the arrangement of these constituents about the Pt atoms in this dimer is clearly an energetically favorable one.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of $[Pt_2(\mathbf{L1})(\mathbf{L2})Cl](PF_6)_2 \cdot 2CH_3CN \cdot H_2O$ is available free of charge via the Internet at http://pubs.acs.org.

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