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Note

Unexpected synthesis and structural characterization of Pt(II)Cl₂-1,5-hexadiene from reaction of allyl chloride and K₂PtCl₄

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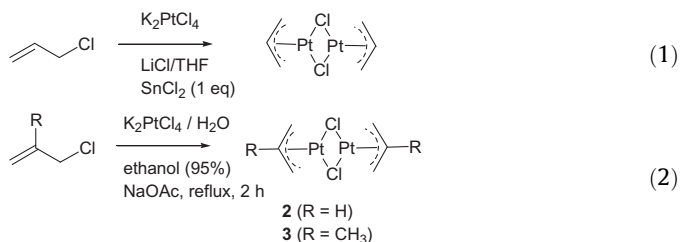
Platinum complexes
X-ray crystal structures
Allyl
Diene

ABSTRACT

An unexpected, new and convenient synthetic procedure for the synthesis of Pt(II)Cl₂-1,5-hexadiene is reported which is done under mild conditions, including a very short reaction time of 10 min. The complex was isolated and crystallized, leading to the first reported crystal structure of the diene complex.

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Allylic complexes of palladium have been known for a long time and also find applications in a wide range organic syntheses [1]. However the attempts to make the analogous platinum complexes had been difficult and low yielding [2] especially until the early 1970s. On the contrary Pt(II)Cl₂-1,5-hexadiene [3] has been known since 1953, but its crystal structure has never been reported. Herein we report a simple and convenient synthetic procedure for the synthesis of Pt(II)Cl₂-1,5-hexadiene and its crystal structure. Lucas and Blom [4] reported the reduction of allylic chlorides and PtCl₂ with SnCl₂, in the presence of LiCl to get π-allyl platinum chloride complex **2** (Eq. (1)). But we were more attracted to Maitlis' [5] synthesis of di-μ-chloro-bis-(η³-2-methylallylplatinum) (**3**) from K₂PtCl₄ and 2-methylallyl chloride (Eq. (2)). We decided to use this procedure for the synthesis of the allyl platinum chloride dimer from allyl chloride and were surprised to make Pt(II)Cl₂-1,5-hexadiene, **1**.



1. Results and discussion

The reaction of K₂PtCl₄ and allyl chloride in the presence of sodium acetate resulted in a complex whose ¹H NMR in CDCl₃ showed five signals each exhibiting ¹⁹⁵Pt satellites with an integral value of 1H, whereas the ¹³C NMR exhibited three signals with two signals exhibiting ¹⁹⁵Pt satellites. This indicated that the complex had five different protons situated on three carbons, which was not in accordance to the expected spectrum of allyl platinum chloride dimer [4,6], with three signals for protons and two signals for carbons. An alternative structure would have been an η¹-allyl platinum species, but that would not explain the splitting of all the protons by the platinum nucleus. gCOSY experiment revealed that four out of the five protons were coupled to one proton, presumably on a central carbon. The NMR solution was transferred to a scintillation vial open to air overnight, leading to formation of crystals, which when dried over P₂O₅ under vacuum and subjected to elemental analysis gave %C = 20.84 and %H = 2.85. This implied that the complex obtained is definitely not η³-allyl platinum chloride dimer nor η¹-allyl platinum chloride dimer, which both are predicted to show %C = 13.25 and %H = 1.85.

Thus, crystals suitable for X-ray diffraction studies were grown by vapor diffusion method using CH₂Cl₂ and hexanes. The details of crystal data are presented in Table 1. A colorless block 0.15 × 0.08 × 0.05 mm in size was mounted on a Cryoloop with Paratone-N oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 s per frame using a scan width of 0.5°.

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Table 1
Crystal data for compound **1**.

Empirical formula	C ₆ H ₁₀ Cl ₂ Pt
Formula weight	348.13
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	11.824(5)
<i>b</i> (Å)	13.219(3)
<i>c</i> (Å)	13.531(3)
α (°)	117.963(3)
β (°)	113.873(4)
γ (°)	91.701(4)
Volume (Å ³)	1644.0(9)
<i>Z</i>	8
<i>D</i> _{calc} (mg/m ³)	2.815
Absorption coefficient (mm ⁻¹)	17.631
<i>F</i> (0 0 0)	1264
Crystal size (mm ³)	0.15 × 0.08 × 0.05
θ Range for data collection (°)	1.81–25.41
Index ranges	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –16 ≤ <i>l</i> ≤ 16
Reflections collected	22995
Independent reflections	6025 [<i>R</i> _{int} = 0.0404]
Completeness to $\theta = 25.75^\circ$	99.9%
Absorption correction	multi-scan/SADABS
Maximum and minimum transmission	0.4158 and 0.1560
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6025/0/325
Goodness-of-fit on <i>F</i> ²	1.024
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0266, <i>wR</i> ₂ = 0.0634
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0660
Largest difference in peak and hole (e Å ⁻³)	1.630 and –2.074

Data collection was 99.9% complete to 25.00° in θ . A total of 22 995 reflections were collected covering the indices, $-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$. About 6025 reflections were found to be symmetry independent, with an *R*_{int} = 0.0404. Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be *P* $\bar{1}$. The data were integrated using the Bruker SHELXTL software program and scaled using the SADABS software program. Solution by Patterson (SHELXS) and all non-hydrogen

atoms were refined anisotropically by full-matrix least-squares on *F*² (SHELXL-97). All hydrogen atoms were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Residual electron density greater than 1e found around Cl and Pt atoms, 1.63e near Cl5, 1.32 near Cl8, 1.28 near Pt1, 1.25 near Cl5 and 1.24 near Pt3 atoms.

X-ray data revealed four independent but very similar molecules in the unit cell (Fig. 1), with eight different Pt–Cl distances in the range 2.2950(18)–2.3202(17) Å and eight distances from metal to alkene C–C bond midpoint in the range 2.0407(0.0259) Å–2.0980(0.0343) Å. Table 2 shows key bond distances and angles involving the central metal for one of the four independent molecules in the unit cell. The Pt atom in **1** is in a distorted square planar environment.

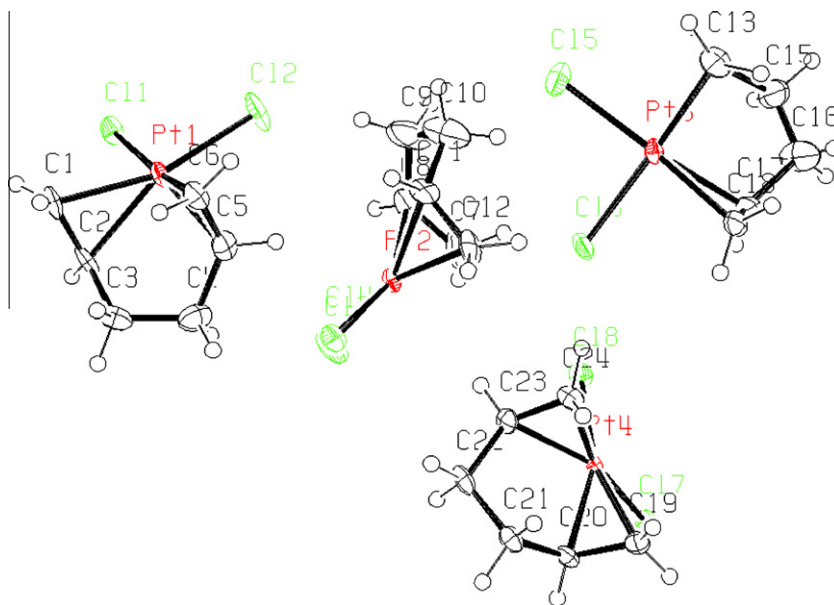
Comparison was done with previous literature data available for the synthesis of **1**, and it was found that although the oldest procedure reported by Jensen [3] seems to be the best in terms of mild conditions and yield (quantitative) but is more time consuming (over 2 days) whereas using our conditions the reaction can be completed in 10 min and using commercially available and cheap reagent, allyl chloride. The unexpected reaction also brings up an interesting route to the product as two molecules of allyl chloride combine to form a bi-allyl which then seems to bind to the metal. This can be hypothetically explained from the balanced equation below (Eq. (3)), wherein two moles of allyl chloride are effectively reduced by one alcohol molecule, forming 1,5-hexadiene (which could be described as bi-allyl) and one

Table 2

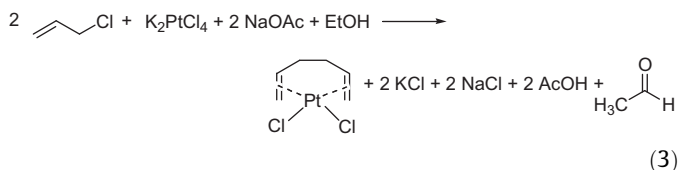
Key bond distances and angles involving the central metal for one of the four independent molecules in the unit cell.

Pt(1)–C(1)	2.194(6)	Cl(2)–Pt(1)–Cl(1)	89.61(6)
Pt(1)–C(2)	2.199(6)	[C(1)C(2)]–Pt(1)–Cl(1)	89.99(92)
Pt(1)–[C(1)C(2)] ^a	2.0974(321)	[C(5)C(6)]–Pt(1)–Cl(2)	89.20(89)
Pt(1)–C(5)	2.187(7)	[C(1)C(2)]–Pt(1)–[C(5)C(6)]	
Pt(1)–C(6)	2.162(7)		
Pt(1)–[C(5)C(6)] ^a	2.0481(322)		
Pt(1)–Cl(2)	2.3119(17)		
Pt(1)–Cl(1)	2.3134(19)		

^a [C(1)C(2)] and [C(5)C(6)] refer to midpoints of the C(1)–C(2) and C(5)–C(6) bonds, respectively.

**Fig. 1.** Crystal structure of compound **1**.

carbonyl double bond, with protonation of two acetates by the hydrogens arising from oxidation of the alcohol.



2. General procedure for synthesis of complex

A scintillation vial was charged with K_2PtCl_4 (0.9561 g, 2.303 mmol), dissolved in deionised water (10 mL) and heated after sealing the cap. To a 250 mL Schlenk flask with a stir bar was added ethanol (120 mL, 95%), **2** (5 mL, 63.1 mmol) and sodium acetate (3.571 g, 43.55 mmol). The turbid solution was then subjected to reflux and once it started refluxing the hot solution in the scintillation vial was transferred to the Schlenk flask via a syringe. The reaction mixture was red in color but over a period of 10 min turned pale yellow. At this point the heating was discontinued and the solvents were evaporated under vacuum. The contents were transferred to a separatory funnel, extracted with CH_2Cl_2 (3×75 mL), organic extracts were collected together and washed with brine (1×100 mL), dried over sodium sulfate, filtered and solvents were evaporated to obtain a pale yellow solid (0.714 g). Crystallization from tetrahydrofuran and hexanes via vapor diffusion gave **1** (0.313 g, 39%) as pale yellow crystals. ^1H NMR (CDCl_3 , 400 MHz) δ 5.73–5.71 (m, 2H), 5.12 (d, $J = 7.6$ Hz, 2H; $J_{\text{PtH}} = 31.9$ Hz), 4.11 (d, $J = 14.0$ Hz, 2H; $J_{\text{PtH}} = 27.9$ Hz), 2.75–2.72 (m, 2H), 2.38–2.28 ppm (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 106.7 ($J_{\text{PtC}} = 64.9$ Hz), 77.9 ($J_{\text{PtC}} = 70.9$ Hz), 32.3 ppm; *Anal. Calc.* for $\text{C}_6\text{H}_{10}\text{Cl}_2\text{Pt}$ (348.13): C, 20.70; H, 2.90. Found: C, 20.84; H, 2.85%.

The aqueous phase remaining after extraction with CH_2Cl_2 was concentrated by rotary evaporation, leaving beige free-flowing solid (11.4 g). A sample of the solid was dissolved in D_2O and the resulting solution analyzed by ^1H and $^{23}\text{Na}\{1\text{H}\}$ NMR spectroscopy,

which showed a very strong ^{23}Na NMR peak at 0.2 ppm but no detectable ^1H NMR resonances other than from HOD. We thus conclude that no organic material was present in the aqueous phase (neither acetate nor acetic acid, which would be lost on rotary evaporation, nor allyl-derived species), and presumably consisted of KCl and NaCl (cf. Eq. (3)).

The crude CH_2Cl_2 -soluble material above (0.714 g) contained no detectable ^{23}Na (NMR) and was mainly complex **1**. In order to determine whether any **2** was present, because no literature ^1H NMR data for **2** could be found, we looked for any peaks with ^1H NMR chemical shifts close to those of the congener, allyl palladium chloride dimer [^1H NMR (CDCl_3 , 500 MHz) δ 7.45–7.43 (m, 2H), 6.02 (d, $J = 6.5$ Hz, 4H), 4.96 ppm (d, $J = 12.5$ Hz, 4H)]. Assuming that the Pt analog **2** has similar NMR data (with the likely exception that Pt satellites would be present as for the hexadiene complex), we can say there is less than 3% of the desired allyl platinum chloride dimer. There are ^1H NMR peaks in the region 2.1–0.8 and 3.7–3.4 ppm which disappear on purification by crystallization. An analysis of the mother liquor by ^1H NMR spectroscopy showed that it contained unidentified material with peaks in the region 2.1–0.8 and 3.7–3.4 ppm, along with approximately 5% of **2**.

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