

**[1,2-Bis(diphenylphosphino)ethane](nitrate)
(trifluoromethylsulfonato)platinum(II)의 합성 및 구조:
[Pt(dppe)(NO₃)(CF₃SO₃)]**

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**Preparation and Structure of [1,2-Bis(diphenylphosphino)ethane]
(nitrate)(trifluoromethylsulfonato)platinum(II):
[Pt(dppe)(NO₃)(CF₃SO₃)]**

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요 약

[Pt(dppe)Cl₂]와 1 당량 AgNO₃ 및 1 당량 AgOTf (OTf = CF₃SO₃)의 순차적 반응으로 표제 착물 [Pt(dppe)(NO₃)(CF₃SO₃)] (dppe = 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂Ph₂)이 합성되었다. Pt 금속은 dppe 리간드의 두 P 원자, nitrate (NO₃⁻) 리간드의 O 원자, 그리고 triflate (trifluoromethylsulfonato, OTf⁻) 리간드의 O 원자로 배위되어 있다. Pt 금속의 배위권은 일그러진 평면 사각형으로 기술될 수 있다.

Abstract

The title complex [Pt(dppe)(NO₃)(CF₃SO₃)] (dppe = 1,2-bis(diphenylphosphino)ethane, Ph₂PCH₂CH₂Ph₂) was prepared by sequentially treating [Pt(dppe)Cl₂] with 1 equiv of AgNO₃ and 1 equiv AgOTf (OTf = CF₃SO₃). The Pt metal is coordinated by two phosphorous atoms of the dppe ligand, one oxygen atom of the nitrate (NO₃⁻) ligand, and one oxygen atom of the triflate (trifluoromethylsulfonato, OTf⁻) ligand. The coordination sphere of Pt metal can be described as a distorted square plane.

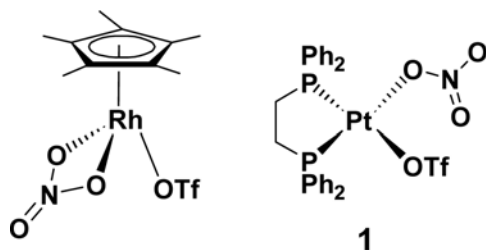
1. Introduction

Transition-metal complexes containing nitrate (NO₃⁻) or triflate (OTf⁻ or CF₃SO₃⁻) ligands have received much attention because they are useful synthetic intermediates.^{1,2)} These ligands are commonly described as labile because they can be readily replaced by other ligands. However, metal complexes possessing both ligands in a single coordination sphere

are quite rare.

We previously reported the preparation and structure of a rhodium(III) complex containing both ligands, [Cp*Rh(η^2 -NO₃)(OTf)], where Cp* is 1,2,3,4,5-pentamethylcyclopentadiene.³⁾ This Rh complex reacted with several alkynes, propargyl halides, thiols, or isocyanates to give interesting products, including cycloaddition adducts of alkynes and triply halide-, thiolato-, or cyanato-bridged

dirhodium complexes.⁴⁻⁶) As a continuation of our research, we decided to prepare group 10 metal complexes containing such labile ligands to investigate similarities and differences in reactivity between those complexes and $[\text{Cp}^*\text{Rh}(\eta^2\text{-NO}_3)(\text{OTf})]$. In this context, we prepared a novel platinum complex, $[\text{Pt}(\text{dppe})(\text{NO}_3)(\text{CF}_3\text{SO}_3)]$ (**1**), where dppe is 1,2-bis(diphenylphosphino)ethane, a chelating bis(phosphine) ligand that is expected to act as a spectator ligand like the Cp* ligand in $[\text{Cp}^*\text{Rh}(\eta^2\text{-NO}_3)(\text{OTf})]$. Herein, we report the preparation and structure of complex **1**.



2. Experimental Section

All reactions were performed under argon. All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. NMR spectra were recorded with a Varian Mercury 300 MHz spectrometer. $[\text{Pt}(\text{dppe})\text{Cl}_2]$ was prepared by the literature method.⁷⁾

Preparation of $[\text{Pt}(\text{dppe})(\text{NO}_3)(\text{CF}_3\text{SO}_3)]$ (1**).** $[\text{Pt}(\text{dppe})\text{Cl}_2]$ (100 mg, 0.151 mmol) and AgNO_3 (26 mg, 0.154 mmol) in a mixed solvent (30 ml) of acetone and dichloromethane ($v:v = 1:1$) were stirred for 6 h at room temperature, and then the solvent was removed under vacuum. The resulting solids were extracted with dichloromethane (30 ml \times 2), and then the solvent was removed. The remaining solid product was washed with hexane

(20 ml \times 2) to give $[\text{Pt}(\text{dppe})(\text{NO}_3)\text{Cl}]$. The subsequent reaction of $[\text{Pt}(\text{dppe})(\text{NO}_3)\text{Cl}]$ with AgOTf (38 mg, 0.148 mmol) in a way similar to the preceding method to give the title complex (72 mg, 59.4%). Recrystallization from dichloromethane/pentane gave colorless crystals. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): δ 8.03~7.96, 7.82~7.73 (20 H, m, Ph), 3.10 (2 H, br, CH_2CH_2), 3.04 (2 H, br, CH_2CH_2), $^3\text{P}\{^1\text{H}\}$ NMR: δ 39.27 ($J_{\text{Pt-P}} = 1930$ Hz). IR (KBr, cm^{-1}): 3440 (br), 1491 (s), 1432 (m), 1383 (m), 1273 (s), 1170 (m), 1104 (m), 981 (m), 721 (m), 635 (m).

X-ray structure determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and intensity data are given

Table 1. X-ray data collection and structure refinement

formula	$\text{C}_{27}\text{H}_{24}\text{F}_3\text{NO}_6\text{P}_2\text{PtS}$
fw	804.56
temperature, K	293(2)
crystal system	triclinic
space group	$P\bar{1}$
a , Å	9.347(2)
b , Å	11.750(2)
c , Å	14.763(3)
α , deg	77.57(2)
β , deg	85.75(2)
γ , deg	67.15(2)
V , Å ³	1459.1(6)
Z	2
d_{cal} , Mg m^{-3}	1.831
μ , mm^{-1}	5.051
T_{min}	0.6042
T_{max}	0.8817
$F(000)$	784
No. of reflections measured	5419
No. of reflections unique	5077
No. of reflections with $I > 2\sigma(I)$	4450
No. of parameters refined	370
2θ range ($^\circ$)	3.5~50.0
GOF (goodness-of-fit on F^2)	1.020
Max., min. in $\Delta\rho$ (e \AA^{-3})	1.801, -1.364
$R1^a$	0.0393
$wR2^b$	0.0939

$$^a R1 = \sum |F_o| - |F| / \sum |F_o|, \quad ^b wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

Table 2. Atomic ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Pt1	2738(1)	1732(1)	2451(1)	48(1)
P1	289(2)	2778(2)	2805(1)	49(1)
P2	2122(2)	69(2)	2630(1)	43(1)
O1	4984(5)	691(5)	2040(3)	62(1)
O2	5802(8)	530(7)	3417(4)	90(2)
O3	7405(6)	-315(6)	2403(5)	85(2)
N1	6107(7)	295(6)	2653(5)	57(2)
C1	-657(9)	4341(7)	2114(6)	63(2)
C2	-927(12)	5398(7)	2459(7)	77(2)
C3	-1627(14)	6575(9)	1913(9)	98(3)
C4	-2076(14)	6711(11)	1053(10)	108(4)
C5	-1800(20)	5706(14)	695(10)	164(8)
C6	-1100(20)	4486(12)	1227(9)	142(6)
C7	103(8)	2889(6)	4012(5)	51(2)
C8	1414(9)	2514(9)	4567(6)	70(2)
C9	1257(11)	2544(10)	5502(7)	84(3)
C10	-193(11)	2992(9)	5880(6)	78(2)
C11	-1484(11)	3365(8)	5338(6)	72(2)
C12	-1348(9)	3306(7)	4409(6)	63(2)
C13	-808(7)	1827(7)	2686(5)	53(2)
C14	176(8)	464(7)	3135(5)	53(2)
C15	2086(8)	-424(6)	1559(4)	49(2)
C16	1171(11)	-1060(9)	1452(6)	75(2)
C17	1224(13)	-1489(11)	638(7)	93(3)
C18	2201(13)	-1273(10)	-57(7)	89(3)
C19	3069(13)	-614(12)	34(7)	97(3)
C20	2987(11)	-165(10)	829(6)	81(3)
C21	3424(8)	-1259(6)	3405(5)	47(2)
C22	4322(9)	-2385(7)	3134(5)	61(2)
C23	5292(10)	-3395(8)	3763(7)	75(2)
C24	5391(10)	-3299(9)	4671(6)	75(2)
C25	4522(10)	-2183(8)	4955(6)	70(2)
C26	3550(9)	-1162(7)	4326(5)	58(2)
C27	3810(30)	5201(18)	1521(15)	226(14)
F1	4640(13)	5838(8)	1409(6)	169(4)
F2	2670(14)	5662(17)	2461(13)	308(11)
F3	2880(19)	5424(9)	896(8)	258(8)
S1	4274(5)	3878(4)	2278(3)	141(2)
O4	3265(10)	3333(7)	2326(9)	162(5)
O5	5361(13)	3690(12)	2889(7)	181(5)
O6	5569(16)	3460(20)	1296(14)	321(13)

in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 19 reflections in the range $15.0^\circ < 2\theta < 25.0^\circ$. The intensity data were empirically corrected for absorption with ψ -scan data. All calculations were carried out with the use

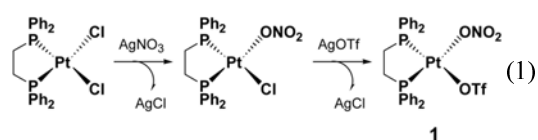
of the SHELXTL programs.⁸⁾

A colorless crystal of complex **1** of approximate dimensions $0.30 \times 0.24 \times 0.22$ mm, shaped as a block, was used for crystal and intensity data collection. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: *P*1 and *P*-1. A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *P*-1. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model. Final atomic coordinates for complex **1** are given in Table 2. Selected bond lengths and angles are given in Table 3.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: CCDC No. 704267 (**1**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3. Results and Discussion

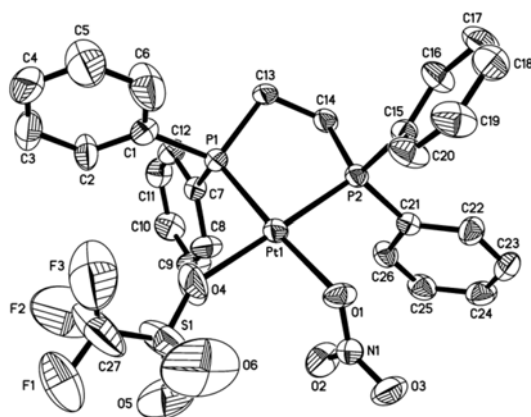
Preparation. Complex **1** was prepared in two steps. In a mixed solvent of acetone and dichloromethane, $[\text{Pt}(\text{dppe})\text{Cl}_2]$ was treated with 1 equiv of AgNO_3 to give $[\text{Pt}(\text{dppe})(\text{NO}_3)\text{Cl}]$, which was subsequently treated with AgOTf to give the final complex $[\text{Pt}(\text{dppe})(\text{NO}_3)(\text{CF}_3\text{SO}_3)]$ (**1**) in 59.4% yield (eq. 1).



Structure. The molecular structure of complex **1** with the atom-labeling scheme is shown Fig. 1, in which the central Pt metal is coordinated to three

Table 3. Selected bond lengths (Å) and bond angles (°)

Pt1-O4	2.091(6)	Pt1-O1	2.100(5)	Pt1-P2	2.203(2)
Pt1-P1	2.222(2)	P1-C13	1.825(7)	P2-C14	1.836(7)
O1-N1	1.310(8)	O2-N1	1.207(8)	O3-N1	1.223(8)
C27-F3	1.23(2)	C27-F1	1.26(2)	C27-F2	1.73(3)
C27-S1	1.63(2)	S1-O4	1.321(7)	S1-O5	1.331(9)
S1-O6	1.843(13)				
O4-Pt1-O1	91.4(3)	O4-Pt1-P2	177.7(3)	O1-Pt1-P1	175.4(1)
P2-Pt1-P1	86.46(7)	N1-O1-Pt1	117.3(4)	O2-N1-O3	124.6(7)
O2-N1-O1	119.0(6)	O3-N1-O1	116.4(6)	F3-C27-F1	117(2)
F3-C27-S1	119(1)	F1-C27-S1	121(1)	F3-C27-F2	105(2)
O4-S1-O5	129.2(8)	O4-S1-C27	113.8(9)	O4-S1-O6	107.9(8)
O5-S1-O6	97.6(8)	C27-S1-O6	76.2(13)	S1-O4-Pt1	151.4(6)

**Fig. 1. The molecular structure of complex 1, showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.**

ligands: dppe, nitrate, and triflate ligands. The coordination sphere of the Pt metal can be described as a distorted square plane. The equatorial plane, defined by P1, P2, O1, O4, and Pt1, is roughly planar with an average atomic displacement of 0.041(4) Å. The Pt-P bond lengths are 2.203(2) and 2.222(2) Å, and Pt-O bond lengths are 2.091(6) and 2.100(5) Å. The O1-Pt-O4 bond angles is 91.4(3)°, which is quite larger than that (85.4(2)°) observed for the related complex [Pt(dppe)(NO₃)₂].⁹⁾

In summary, we prepared the Pt-dppe complex [Pt(dppe)(NO₃)(CF₃SO₃)] that contains two labile ligands, nitrate and triflate ligands. X-ray structural study of this complex revealed that it has an η^1 -

NO₃ ligand.

Acknowledgement

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