

Preparation and Structure of *trans*-Bis(*tert*-butylamine)dichloropalladium(II), *trans*-[PdCl₂(*t*-BuNH₂)₂]

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trans-Bis(*tert*-butylamine)dichloropalladium(II), *trans*-[PdCl₂(*t*-BuNH₂)₂]의 합성 및 구조

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Abstract

Compound PdCl₂(PhCN)₂ (**1**) reacted with *tert*-butylamine (*t*-BuNH₂) to give *trans*-[PdCl₂(*t*-BuNH₂)₂] (**2**). Compound **2** was characterized by spectroscopy (¹H-NMR, ¹³C{¹H}-NMR, and IR) and X-ray diffraction. Crystallographic data for **2**: monoclinic space group *P*2₁/*c*, *a* = 6.298(1) Å, *b* = 20.740(2) Å, *c* = 10.731(1) Å, β = 92.58(1)°, *Z* = 4, *R*(*wR*₂) = 0.0207(0.0543).

요 약

화합물 PdCl₂(PhCN)₂(**1**)와 *tert*-butylamine이 반응하여 *trans*-[PdCl₂(*t*-BuNH₂)₂] (**2**)가 생성되었다. 화합물 **2**의 구조가 분광학적 방법(¹H-NMR, ¹³C{¹H}-NMR, IR) 및 X-ray 회절법으로 규명되었다. 화합물 **2**의 결정학 자료: 단사정계 공간군 *P*2₁/*c*, *a* = 6.298(1) Å, *b* = 20.740(2) Å, *c* = 10.731(1) Å, β = 92.58(1)°, *Z* = 4, *R*(*wR*₂) = 0.0207(0.0543).

1. Introduction

Transition-metal-imido (or nitrene, L_nM=NR) complexes have been of continuous interest¹⁻⁷. Metal-amido (L_nM-NHR) complexes have often been employed to prepare imido complexes by deprotonation of the N-H protons with strong bases. So far, group 10 metal-imido complexes have not been reported (L_nM=NR: M=Ni, Pd, or Pt). In an attempt to prepare Pd-imido complexes, we prepared a palladium-amine compound {*trans*-[PdCl₂(*t*-BuNH₂)₂]} as a precursor, which would then be further treated with strong bases, such as *n*-BuLi, *t*-BuLi, Na[N(SiMe₃)₂], and Na[N(SiMe₃)₂]. Herein we report the preparation and structure of *trans*-[PdCl₂(*t*-BuNH₂)₂].

2. Experimental Section

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use. Glassware was either flame- or oven-dried. Hydrocarbon solvents were stirred over concentrated H₂SO₄ for about 48 h, neutralized with K₂CO₃, stirred over sodium metal, and distilled by vacuum transfer. Benzene and toluene were stirred over sodium metal and distilled by vacuum transfer. Dichloromethane was stirred over CaH₂ and dis-

tiled by vacuum transfer. NMR solvent (CDCl_3) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. *tert*-Butylamine was purchased from Aldrich company. $\text{PdCl}_2(\text{PhCN})_2$ (**1**) was prepared by the literature method⁸⁾.

^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. IR spectra were recorded with a Nicolet 205 FT-IR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration.

Preparation of trans-[$\text{PdCl}_2(\text{t-BuNH}_2)_2$] (**2**).

Compound **1** (0.10 g, 0.261 mmol) and *tert*-butylamine (0.060 ml, 0.574 mmol) in toluene (30 ml) was stirred for 30 min at room temperature, and then the solvent was removed under vacuum. The resulting solids were washed with hexanes (20 ml \times 2), and then dried under vacuum to give 0.084 g (0.164 mmol, 63.1%) of compound **2**. This product was recrystallized from benzene-hexane to give yellow crystals.

^1H -NMR (CDCl_3): δ 1.45 (18H, s, *t*-Bu), 2.78 (4H, s, NH_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): δ 32.30 (*t*-Bu). mp: 250–252°C. IR (KBr): 3247, 3211, 3129 (N-H), 2970, 2928, 2903, 2870, 1575, 1472, 1397, 1215, 899 cm^{-1} .

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 28 reflections in the range $10.0^\circ < 2\theta < 25.0^\circ$. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with Ψ -scan data. All calculations were carried out with use of the *SHELXL-97* programs⁹⁾.

A yellow crystal of **1**, shaped as a block of

Table 1. X-ray data collection and structure refinement

empirical formula	$\text{C}_8\text{H}_{22}\text{N}_2\text{Cl}_2\text{Pd}$
fw	323.53
temperature, K	295(2)
crystal system	monoclinic
space group	$P2_1/c$
<i>a</i> , Å	6.298(1)
<i>b</i> , Å	20.740(2)
<i>c</i> , Å	10.731(1)
β , deg	92.58(1)
<i>V</i> , Å ³	1400.2(3)
<i>Z</i>	4
d_{calc} , g cm ⁻³	1.535
μ , mm ⁻¹	1.674
<i>F</i> (000)	656
T_{min}	0.2941
T_{max}	0.7364
2θ range (°)	3.550
scan type	ω
scan speed	variable
No. of reflns measured	2689
No. of reflns unique	2456
No. of reflns with $I > 2\sigma(I)$	2323
No. of params refined	135
Max. in $\Delta\rho$ (eÅ ⁻³)	0.301
Min. in $\Delta\rho$ (eÅ ⁻³)	0.251
<i>GOF</i> on F^2	1.068
<i>R</i>	0.0207
wR_2^a	0.0543

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

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Pd(1)	1561(1)	7395(1)	6335(1)	39(1)
Cl(1)	4113(1)	7769(1)	5025(1)	60(1)
Cl(2)	-1023(1)	7005(1)	7605(1)	58(1)
N(1)	3615(3)	6683(1)	6996(2)	44(1)
N(2)	-481(3)	8113(1)	5717(2)	44(1)
C(1)	3756(4)	6026(1)	6407(2)	56(1)
C(2)	4870(7)	6103(2)	5178(3)	90(1)
C(3)	5100(5)	5594(2)	7285(3)	79(1)
C(4)	1541(5)	5741(2)	6191(4)	91(1)
C(5)	-575(4)	8760(1)	6355(3)	59(1)
C(6)	-1973(6)	9204(2)	5529(4)	85(1)
C(7)	-1573(8)	8667(2)	7604(3)	104(1)
C(8)	1631(5)	9039(2)	6511(5)	105(1)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

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

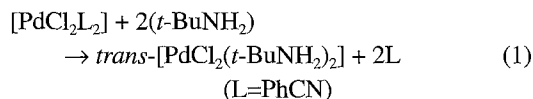
Pd1-N2	2.058(2)	Pd1-N1	2.067(2)	Pd1-Cl2	2.3152(6)
Pd1-Cl1	2.3153(6)	N1-C1	1.507(3)	N2-C5	1.508(3)
N2-Pd1-N1	178.69(8)	N2-Pd1-Cl2	89.80(6)	N1-Pd1-Cl2	89.66(6)
N2-Pd1-Cl1	90.18(6)	N1-Pd1-Cl1	90.39(6)	Cl2-Pd1-Cl1	178.56(3)
C1-N1-Pd1	123.4(2)	C5-N2-Pd1	122.3(2)		

approximate dimensions $0.36 \times 0.32 \times 0.28 \text{ nm}^3$, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $h0l$ ($l=2n+1$) and $0k0$ ($k=2n+1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The NH_2 hydrogen atoms were located in the difference Fourier maps. The remaining hydrogen atoms were generated in ideal positions and refined in a riding mode.

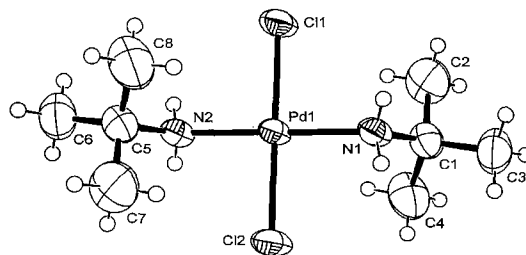
Details on crystal data and intensity data are given in Table 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Tables 2 and 3, respectively.

3. Results and Discussion

Preparation. A *trans* [Pd(II)-bis(amine)] complex, *trans*-[PdCl₂(*t*-BuNH₂)₂] (**2**), has been prepared by replacing the labile benzonitrile ligands in [PdCl₂(PhCN)₂] (**1**) with *tert*-butylamine in toluene in moderate yield (eq. 1). During the reaction, an initially orange solution turned to a yellow one. The solid product was recrystallized from benzene-hexane to give X-ray quality crystals.



Compound **2** is stable both in solution and in the solid state. As expected, this compound exhibits a

**Fig. 1. An ORTEP drawing of 2 with the atom-labeling scheme and 50% probability thermal ellipsoids.**

singlet at $\delta=1.45$ ppm for *tert*-butyl protons in its ¹H-NMR spectrum and also a singlet at $\delta=32.30$ ppm for *tert*-butyl carbons in its ¹³C{¹H}-NMR spectrum. However, we could not observe the peaks corresponding to the quaternary carbons in *tert*-butyl groups. The N-H stretching modes appear in the range of $3247\sim 3129 \text{ cm}^{-1}$ in the IR spectrum.

Structure. The structure of compound **2** with the atom-numbering scheme is shown in Fig. 1. The coordination sphere of the Pd metal can be described as a square plane, with two *trans* *t*-BuNH₂ ligands and also with two *trans* Cl ligands. The bond angles of N-Pd-N and Cl-Pd-Cl are $178.69(8)^\circ$ and $178.56(3)^\circ$, respectively. The formal oxidation of the Pd metal is +2, and its electron count is 16. The equatorial plane, defined by Pd1, Cl1, Cl2, N1, and N2 atoms, is relatively planar with the atomic displacement not exceeding 0.0252 \AA .

All bond distances and bond angles are normal

Table 4. Hydrogen bonding parameters (Å, °)

Bond	D-H	H...A	D-H...A	D...A	Position of A
N1-HN1A...Cl1	0.886	2.730	138.52	3.444	$x, -y+3/2, z+1/2$
N1-HN1B...Cl2	0.771	2.742	159.57	3.475	$x+1, y, z$
N2-HN2A...Cl1	0.763	2.809	157.26	3.525	$x-1, y, z$
N2-HN2B...Cl2	0.882	2.546	151.88	3.351	$x, -y+3/2, z-1/2$

within experimental error. For example, the Pd-N bond distances (2.058(2) and 2.067(3) Å) indicate a Pd-N single bond, which is expected to lie within 1.95~2.15 Å.¹⁰⁾ All of the NH₂ hydrogen atoms are involved in intermolecular hydrogen bonds of the type N-H···Cl. The hydrogen-bonding parameters (Table 4) indicate relatively weak hydrogen bonds.

In summary, we have prepared and structurally characterized *trans*-[PdCl₂(*t*-BuNH₂)₂] from the reaction of [PdCl₂(PhCN)₂] with *tert*-butylamine in a mole ratio of 1:1.

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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