Korean J. Crystallography
Vol. 12, No. 3, pp.137~140, 2001

Synthesis and Structure of *trans*-Dichlorobis(diisopropylaniline)palladium(II), *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$]

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trans-Dichlorobis(diisopropylaniline)palladium(II), *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$]의 합성 및 구조

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Abstract

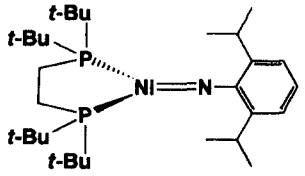
Compound $PdCl_2(PhC{\equiv}N)_2$ (**1**) reacted with 2,6-diisopropylaniline to give *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$] (**2**). Compound **2** was characterized by spectroscopy (^{1}H-NMR, ^{13}C-NMR, and IR) and X-ray diffraction. Crystallographic data for **2**: monoclinic space group $P2_1/n$, a = 13.532(3) Å, b = 5.749(1) Å, c = 17.880(4) Å, β = 103.84(2)°, Z = 2, $R(wR_2)$ = 0.0466(0.1226).

요 약

화합물 $PdCl_2(PhC{\equiv}N)_2$ (**1**)와 2,6-diisopropylaniline이 반응하여 *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$] (**2**)가 합성되었다. 화합물 **2**의 구조가 분광학적 방법(^{1}H-NMR, ^{13}C-NMR, IR) 및 X-ray 회절법으로 규명되었다. 화합물 **2**의 결정학 자료 : 단사정계 공간군 $P2_1/n$, a = 13.532(3) Å, b = 5.749(1) Å, c = 17.880(4) Å, β = 103.84(2)°, Z = 2, $R(wR_2)$ = 0.0466(0.1226).

1. Introduction

Transition-metal-imido complexes have got continuous attractions[1-7]. For example, they have played an important role in biological processes such as nitrogen fixation and also in industrial processes[8,9]. The chemistry of late-transition-metal complexes possessing amide (NR^{2-}) and imido (NR^{2-}) ligands is much less developed than that of early- and mid-transition-metal complexes, primarily because of the lack of a general synthetic method. Very recently, Hillhouse and co-workers reported the preparation of a terminal imido complex of nickel, (dtbpe)Ni(N-C_6H_3-2,6-*i*-Pr_2) {dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane}, which is the first metal-imido complex of group 10 metals (Ni, Pd, and Pd)[10].



(dtbpe)Ni(N-C_6H_3-2,6-*i*-Pr_2)

In an attempt to prepare Pd-imido complexes, we set out to prepare a palladium-aniline compound *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$] as a precursor, which would then be treated further with strong bases such as *t*-BuLi, *n*-BuLi, Li[$N(SiMe_3)_2$], Na[$N(SiMe_3)_2$], and [Ph_3C][PF_6]. Herein, we report the synthesis

and structure of *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_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 H_2SO_4 for about 48 h, neutralized with K_2CO_3, stirred over sodium metal, and distilled by vacuum transfer. Toluene was stirred over sodium metal and distilled by vacuum transfer. Dichloromethane was stirred over CaH_2 and distilled by vacuum transfer. NMR solvent ($CDCl_3$) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. 2,6-Diisopropylaniline was purchased from Aldrich company. $PdCl_2(PhCN)_2$ (**1**) was prepared by the literature method[11].

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane (TMS). 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*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$] (2). Compound **1** (0.335 g, 0.873 mmol) and excess 2,6-diisopropylaniline (0.66 m*l*, 3.492 mmol) in toluene (50 m*l*) were stirred for 24 h at room temperature, and then the solvent was removed under vacuum. The resulting solids were washed with hexane (30 m*l*×2) and pentane (30 m*l*×2), and then dried under vacuum to give a yellow powder of compound **2** (0.22 g, 0.414 mmol, 49%). This product was recrystallized from dichloromethane-hexane.

^{1}H-NMR ($CDCl_3$): δ 1.34 (24H, s, $CH(CH_3)_2$), 3.55 (4H, septet, $CH(CH_3)_2$), 4.73 (4H, s, NH_2), 7.12 (4H, d, aniline β-H), 7.19 (2H, t, aniline γ-H). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 28.93~24.23 (*i*-Pr), 124.31~140.49 (Ph). mp: 220~222°C. IR (KBr): 3301 (N-H), 3245 (N-H), 2962, 2926, 2669, 1569, 1462, 1101, 798, 753 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 19 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 for absorption with Ψ-scan data. All calculations were carried out with use of the SHELXTL programs[12].

A yellow crystal of **2**, shaped as a block of approximate dimensions 0.28×0.20×0.18 mm^3, was

Table 1. X-ray data collection and structure refinement

empirical formula	$C_{24}H_{38}N_2Cl_2Pd$
fw	531.86
temperature, K	295(2)
crystal system	monoclinic
space group	$P2_1/n$
a, Å	13.532(3)
b, Å	5.749(1)
c, Å	17.880(4)
β, deg	103.84(2)
V, Å^3	1350.7(5)
Z	2
d_{cal}, g cm^{-1}	1.308
μ, mm^{-1}	0.897
F(000)	552
T_{min}	0.6086
T_{max}	0.6854
2θ range (°)	3.5~50
scan type	ω
scan speed	variable
No. of reflns measured	2454
No. of reflns unique	2348
No. of reflns with $I > 2\sigma(I)$	1865
No. of params refined	120
Max. in (e Å^{-3})	0.661
Min. in (e Å^{-3})	−0.571
GOF on F^2	1.068
R	0.0466
wR_2^a	0.1226

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

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3)

	x	*y*	*z*	*U*(eq)[a]
Pd(1)	5000	0	5000	48(1)
Cl(1)	5762(1)	−2755(2)	5897(1)	72(1)
N(1)	4465(4)	1978(8)	5793(2)	59(1)
C(1)	4078(4)	789(10)	6379(3)	62(1)
C(2)	3143(5)	−367(11)	6157(4)	77(2)
C(3)	2814(6)	−1576(16)	6738(4)	106(3)
C(4)	3367(8)	−1629(19)	7474(5)	128(3)
C(5)	4264(8)	−462(16)	7679(4)	107(3)
C(6)	4670(5)	772(12)	7143(3)	77(2)
C(7)	2492(6)	−357(13)	5355(5)	84(2)
C(8)	1443(8)	630(19)	5300(6)	141(4)
C(9)	2491(10)	−2600(20)	4970(6)	168(4)
C(10)	5667(6)	2023(14)	7379(4)	92(2)
C(11)	5549(11)	4110(20)	7773(8)	184(5)
C(12)	6532(12)	430(20)	7856(8)	181(6)

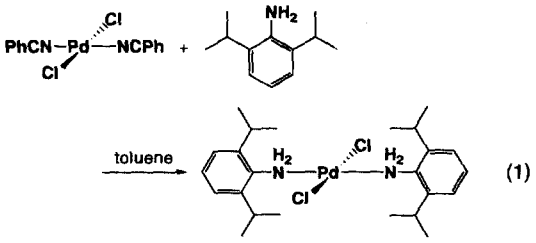
[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences, *h*0*l* ($h + l = 2n + 1$) and 0*k*0 ($k = 2n + 1$), unambiguously indicated $P2_1/n$ as a space group. The structure was solved by direct methods. The isopropyl substituents exhibited an extreme structural disorder, and therefore they were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. The NH_2 hydrogen atoms were located in the difference Fourier maps. The other 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-bis(amine) compound, *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$] (**2**), has been prepared by replacing the labile benzonitrile ligands in $PdCl_2(PhCN)_2$ (**1**) with 2,6-diisopropylaniline in toluene (eq. 1). During the reaction, an initially orange solution slowly turned to a yellow one. The solid product was recrystallized from dichloromethane-hexane to give yellow crystals.



(1)

Compound **2** appears to be air- and moisture-stable both in solution and in the solid state. The isopropyl fragment exhibits a doublet at 1.34 ppm for methyl protons ($CH(CH_3)_2$) and a septet for δ 3.55 ppm for methynyl proton ($CH(CH_3)_2$) in the ^{1}H-NMR spectrum. The phenyl protons in the 2,6-diisopropylaniline ligand resonate at δ 7.12 ppm (β-H) and at δ 7.19 ppm (γ-H). $^{13}C\{^1H\}$-NMR spectra of compound **2** exhibit peaks at δ 28.93~24.23 ppm for isopropyl carbons. As expected, the N-H stretching modes appear at 3301 and 3245 cm^{-1} in the IR spectrum.

Structure. The molecular structure of compound **1** with the atom-numbering scheme is shown in Fig. 1. The Pd metal lie on the crystallographic center of symmetry, which explains why this compound has the *Z* value of 2 instead of 4. The coordination sphere of palladium can be described as square planar, with two *trans* chloride ligands and two *trans* 2,6-diisopropylaniline ligands. The palladium metal has a formal oxidation state of +2, and therefore it has a formal electron count of 16. The equatorial plane, defined by Pd1, N1, N1#1, Cl1, and Cl1#1 (#1 = $-x + 1$, $-y$, $-z + 1$), is perfectly planar due to

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

Pd1-N1	2.078(4)	Pd1-Cl1	2.313(1)	N1-C1	1.451(7)
N1#1-Pd1-N1	180.0(2)	N1#1-Pd1-Cl1	85.9(1)	N1-Pd1-Cl1	94.1(1)
C1-N1-Pd1	118.7(3)				

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1$, $-y$, $-z + 1$.

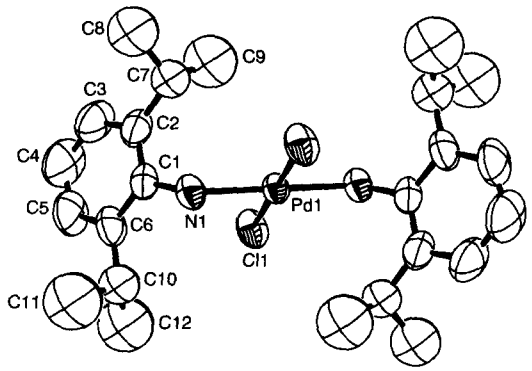


Fig. 1. An ORTEP drawing of 2 with the atom-labeling scheme and 50% probability thermal ellipsoids.

its generation by symmetry operation. The benzene ring in the 2,6-diisopropylaniline ligand is essentially planar with the average atomic displacement of 0.0057 Å and has the dihedral angle of 75.3(2)° with respect to the equatorial plane.

All bond distances and bond angles are normal within experimental error. For example, the PdN bond distance (2.078(4) Å) indicates a PdN single bond, which is expected to lie within 1.95~2.15 Å[13]. One of the NH_2 hydrogen atoms in the 2,6-diisopropylaniline ligand is involved in the intermolecular hydrogen bond of the type N-H···Cl: N1-HN1 = 0.932 Å, N1···Cl1 = 3.482 Å, HN1···Cl1 = 2.700 Å, and N1-HN1···Cl1 = 142.03°. The bonding parameters of this hydrogen bond indicates a relatively weak hydrogen bond.

In summary, we have structurally characterized *trans*-[Pd(NH_2-C_6H_3-2,6-*i*-Pr_2)$_2$$Cl_2$], which was prepared by the reaction of [$PdCl_2$(PhCN)$_2$] with excess 2,6-diisopropylaniline.

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.

Acknowledgment

This work is based on research sponsored by the Korea Research Foundation Grant (KRF-2000-015-DP0262).

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