

단 신

**N-H...O 수소 결합으로 연결된 3합체: Diphenyl(*tert*-butylamino)-  
phosphine oxide, {O=PPh<sub>2</sub>(NH-*t*-Bu)}<sub>3</sub>의 구조**

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**N-H...O Hydrogen-Bonded Trimer: Structure of Diphenyl(*tert*-butylamino)-  
phosphine oxide, {O=PPh<sub>2</sub>(NH-*t*-Bu)}<sub>3</sub>**

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**INTRODUCTION**

Transition-metalimido (or nitrene, L<sub>n</sub>M=NR) complexes have been of continuous interest.<sup>1-6</sup> Metal chlorides have frequently been employed to prepare imido complexes by reactions with primary amines (RNH<sub>2</sub>) or lithium amides (LiNH-*t*-Bu). We tried to prepare Rh-imido complexes by treating rhodium(I) chloride (RhCl(PPh<sub>3</sub>)<sub>3</sub>) and lithium amide (LiNH-*t*-Bu). From this reaction, however, we isolated diphenyl(*tert*-butylamino)phosphine oxide, O=PPh<sub>2</sub>(NH-*t*-Bu), three molecules of which are linked through the N-H...O hydrogen bonding to form a trimeric structure. Herein we report the structure of {O=PPh<sub>2</sub>(NH-*t*-Bu)}<sub>3</sub>.

**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, and it was either flame-dried or oven-dried. Hydrocarbon solvents were stirred over concentrated H<sub>2</sub>SO<sub>4</sub> for about 48 h, neutralized with K<sub>2</sub>CO<sub>3</sub>, stirred over sodium metal, and distilled by vacuum transfer. Diethyl ether, tetra-

hydrofuran (THF) were stirred over sodium metal and distilled by vacuum transfer. The NMR solvent (CDCl<sub>3</sub>) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Chlorotris(triphenylphosphine)rhodium(I) (RhCl(PPh<sub>3</sub>)<sub>3</sub>), *tert*-butylamine (NH<sub>2</sub>-*t*-Bu), and *n*-butyllithium (*n*-BuLi) were purchased from Aldrich company. Lithium *n*-butyl amide (LiNH-*n*-Bu) was prepared by treating *tert*-butylamine with *n*-butyllithium in THF.

<sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. <sup>31</sup>P-NMR spectra were also recorded with a Varian Unity Inova 500 MHz spectrometer with reference to external 85% H<sub>3</sub>PO<sub>4</sub>. IR spectra were recorded with a Nicolet 205 FT-IR spectrophotometer.

**Isolation of O=PPh<sub>2</sub>(NH-*t*-Bu) (1).** To 30 mL of THF containing 0.10 g (0.25 mmol) of RhCl(PPh<sub>3</sub>)<sub>3</sub> was added 0.08 g (1.0 mmol) of LiNH-*t*-Bu. The resultant solution was stirred for 1 h at 0 °C and then filtered. During stirring, a dark red solution turned to a black-red one. The solvent was removed under vacuum to give black-red solids. The resultant solids were extracted with pentane (20 mL 2), and then dried under vacuum to give 0.094 g (0.75 mmol, 52%) of O=PPh<sub>2</sub>(NH-*t*-Bu) (1). The product was recrystallized from pentane at room temperature.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.41 (10H, m, Ph), 2.78 (11H, s, NH), 1.29 (9H, s, *t*-Bu). <sup>13</sup>C {<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ 132.53, 132.46, 132.06, 129.07, 128.98 (Ph), 33.04 (*t*-Bu). <sup>31</sup>P-NMR (CDCl<sub>3</sub>): δ 20.025. IR (KBr): 3204 (NH), 2954, 2922, 2855, 1461, 1426, 1384, 1225, 1184 (P=O), 1111, 1039, 1018, 855, 723, 694, 567, 524 cm<sup>-1</sup>.

**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 24 reflections in the range 10.0 · 2θ · 25.0°. Three check-reflections were measured every 100 reflections throughout data collection. Intensity data were corrected for Lorentz 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 SHELXTL programs.<sup>3</sup>

A yellow crystal of **1**, shaped as a block of approximate dimensions 0.44 · 0.34 · 0.32 mm<sup>3</sup>, was used for crystal and intensity data collection. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: *P*<sup>1</sup> and *P*<sup>1</sup> $\bar{1}$ . A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *P*<sup>1</sup> $\bar{1}$ . The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. N-H hydrogen atoms were located and refined isotropically. The remaining hydrogen atoms were generated in ideal positions.

Details on crystal data and intensity data are given in Table 1. Final atomic positional parameters for non-hydrogen atoms are shown in Table 2. The selected bond distances and bond angles are shown in Table 3.

## RESULTS AND DISCUSSION

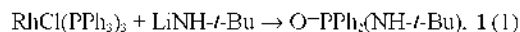
A phosphine oxide compound O-PPh<sub>2</sub>(NH-*t*-Bu) (**1**) was isolated from the reaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> and (LiNH-*t*-Bu) in moderate yield (52%) (eq 1). The oxygen atom in compound **1** has probably been incorporated by air-oxidation during recrystallization. However, we cannot rule out the possibility that the trace amount of water, present in the crystallization solvent (pentane), has reacted with the reaction product to give the title compound. Unfortunately, we cannot give reasonable expla-

Table 1. X-ray data collection and structure refinement

empirical formula	C <sub>16</sub> H <sub>20</sub> NOP
fw	273.30
temperature, K	295(2)
crystal system	triclinic
space group	<i>P</i> <sup>1</sup> $\bar{1}$
<i>a</i> , Å	9.993(4)
<i>b</i> , Å	16.812(7)
<i>c</i> , Å	16.969(6)
α, deg	119.15(2)
β, deg	90.57(2)
γ, deg	105.62(1)
<i>V</i> , Å <sup>3</sup>	2364(2)
<i>Z</i>	6
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.152
μ, mm <sup>-1</sup>	0.167
<i>F</i> (000)	876
<i>T</i> <sub>min</sub>	0.7102
<i>T</i> <sub>max</sub>	0.9179
2θ range (°)	3.5~50
scan type	ω
scan speed	variable
No. of reflns measured	8176
No. of reflns unique	7694
No. of reflns with <i>I</i> > 2σ( <i>I</i> )	5651
No. of params refined	527
Max. in Δρ (eÅ <sup>-3</sup> )	0.185
Min. in Δρ (eÅ <sup>-3</sup> )	-0.203
<i>GOF</i> on <i>F</i> <sup>2</sup>	1.007
<i>R</i>	0.0440
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.1044

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

nations for these unusual observations: (1) P-N bond formation and (2) the unusual stoichiometry.



Compound **1** has been characterized by NMR (<sup>1</sup>H-, <sup>13</sup>C {<sup>1</sup>H}-, and <sup>31</sup>P-NMR), IR spectroscopy, and X-ray diffraction. In the <sup>1</sup>H-NMR spectrum, *tert*-butyl protons appear as a singlet at δ 1.29 ppm. As expected, the <sup>31</sup>P-NMR spectrum shows a singlet for PPh<sub>3</sub> at δ 20.03 ppm. In the IR spectrum, the P=O band appears at 1184 cm<sup>-1</sup> and the N-H band at 3204 cm<sup>-1</sup>.

The structure of the hydrogen-bonded trimer with the atom-numbering scheme is shown in Fig. 1 and that of

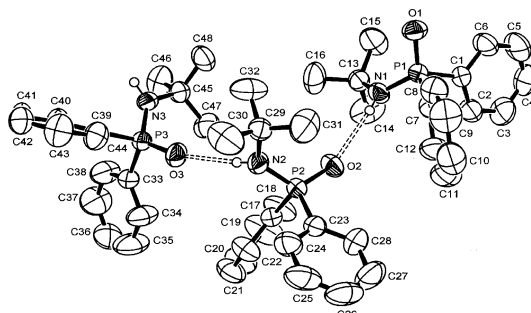
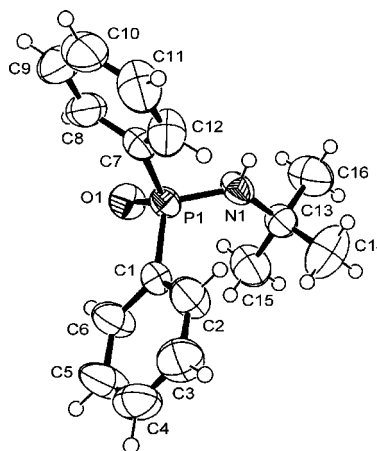
Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \cdot 10^3$ )

	x	y	z	$U(\text{eq})^a$
P(1)	8958(1)	3858(1)	2484(1)	46(1)
P(2)	5865(1)	1516(1)	-1005(1)	48(1)
P(3)	7708(1)	2441(1)	-3585(1)	47(1)
O(1)	9420(2)	4924(1)	2956(1)	62(1)
O(2)	6879(2)	1836(1)	-180(1)	64(1)
O(3)	6825(2)	2268(1)	-2948(1)	63(1)
N(1)	9201(2)	3255(2)	1428(1)	56(1)
N(2)	5795(2)	2291(1)	-1311(1)	55(1)
N(3)	9329(2)	3156(2)	-3185(1)	55(1)
C(1)	9818(2)	3511(2)	3167(2)	49(1)
C(2)	9665(3)	2564(2)	2893(2)	76(1)
C(3)	10325(4)	2337(3)	3442(2)	92(1)
C(4)	11139(4)	3031(3)	4256(2)	88(1)
C(5)	11298(4)	3957(3)	4538(2)	103(1)
C(6)	10634(3)	4207(2)	4001(2)	77(1)
C(7)	7080(2)	3382(2)	2424(2)	52(1)
C(8)	6338(3)	4031(2)	2836(2)	71(1)
C(9)	4908(3)	3714(3)	2860(2)	92(1)
C(10)	4219(3)	2764(3)	2487(2)	95(1)
C(11)	4930(3)	2107(3)	2083(2)	95(1)
C(12)	6355(3)	2408(2)	2039(2)	79(1)
C(13)	10544(2)	3292(2)	1054(2)	57(1)
C(14)	10821(4)	2353(3)	740(3)	111(1)
C(15)	11775(3)	4124(3)	1767(2)	95(1)
C(16)	10365(3)	3443(3)	253(2)	98(1)
C(17)	6212(3)	555(2)	-2021(2)	51(1)
C(18)	7467(3)	393(2)	-1989(2)	90(1)
C(19)	7751(4)	-371(3)	-2726(3)	124(2)
C(20)	6773(4)	-973(2)	-3491(2)	99(1)
C(21)	5520(4)	-835(2)	-3544(2)	90(1)
C(22)	5228(3)	-69(2)	-2814(2)	78(1)
C(23)	4092(3)	979(2)	-899(2)	56(1)
C(24)	2893(3)	890(2)	-1404(2)	76(1)
C(25)	1560(3)	408(2)	-1360(3)	99(1)
C(26)	1394(4)	5(3)	-835(3)	107(1)
C(27)	2546(5)	72(3)	-334(3)	109(1)
C(28)	3902(3)	568(2)	-354(2)	81(1)
C(29)	5656(3)	3268(2)	-734(2)	56(1)
C(30)	4523(4)	3355(3)	-1256(3)	112(1)
C(31)	5272(5)	3433(2)	186(2)	115(1)
C(32)	7032(3)	4003(2)	-598(3)	100(1)
C(33)	7773(3)	1300(2)	-4525(2)	53(1)
C(34)	6833(4)	465(2)	-4666(2)	88(1)
C(35)	6834(5)	-416(2)	-5404(3)	119(1)
C(36)	7749(5)	-467(2)	-5991(2)	99(1)
C(37)	8706(5)	348(3)	-5847(2)	116(1)
C(38)	8711(4)	1230(2)	-5127(2)	92(1)

Table 2. (continued)

	x	y	z	$U(\text{eq})^a$
C(39)	6924(2)	2969(2)	-4102(2)	48(1)
C(40)	7440(3)	3132(2)	-4790(2)	66(1)
C(41)	6739(3)	3481(2)	-5196(2)	76(1)
C(42)	5533(3)	3690(2)	-4919(2)	77(1)
C(43)	5011(3)	3542(2)	-4244(2)	86(1)
C(44)	5700(3)	3174(2)	-3845(2)	69(1)
C(45)	10479(3)	3111(2)	-2659(2)	59(1)
C(46)	11758(3)	3138(3)	-3140(2)	93(1)
C(48)	10836(4)	3991(2)	-1696(2)	86(1)

<sup>a</sup>Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Fig. 1. ORTEP drawing of  $\{O=PPh(NH-t-Bu)\}_3$ , showing the atom-labeling scheme and 50% probability thermal ellipsoids.Fig. 2. ORTEP drawing of  $O=PPh(NH-t-Bu)$ .

the constituent molecule (or formula unit) in Fig. 2. One asymmetric unit contains three molecules linked by hydrogen bonds, and therefore the unit cell has  $Z=6$

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

P1-O1	1.489(2)	P2-O2	1.490(2)	P3-O3	1.489(2)
P1-N1	1.634(2)	P2-N2	1.637(2)	P3-N3	1.632(2)
P1-C7	1.811(3)	P2-C23	1.814(3)	P3-C39	1.815(2)
P1-C1	1.825(2)	P2-C17	1.817(2)	P3-C33	1.821(2)
N1-C13	1.489(3)	N2-C29	1.494(3)	N3-C45	1.490(3)
O1-P1-N1	118.6(1)	O2-P2-N2	119.1(1)	O3-P3-N3	119.1(1)
O1-P1-C7	110.9(1)	O2-P2-C23	110.3(1)	O3-P3-C39	110.7(1)
N1-P1-C7	103.8(1)	N2-P2-C23	107.5(1)	N3-P3-C39	103.4(1)
O1-P1-C1	108.5(1)	O2-P2-C17	111.1(1)	O3-P3-C33	109.5(1)
N1-P1-C1	108.1(1)	N2-P2-C17	103.6(1)	N3-P3-C33	107.2(1)
C7-P1-C1	106.3(1)	C23-P2-C17	104.0(1)	C39-P3-C33	106.1(1)
C13-N1-P1	128.9(2)	C29-N2-P2	128.3(2)	C45-N3-P3	128.6(2)

Table 4. Hydrogen bonding parameters (Å, °)

Bond	D...H	H-A	D...H-A	D...A	Position of A
N1-HN1...O2	0.741	2.284	167.59	3.012	intramolecular
N2-HN2...O3	0.823	2.153	166.37	2.959	intramolecular
N3-HN3...O1	0.825	2.160	161.06	2.953	$x + 2, y - 1, z$

instead of *Z*-2. All three molecules constituting the asymmetric unit have essentially the same bonding parameters (Table 3). The geometry of each molecule can be described as a tetrahedron, in which the phosphorus atom is a central atom and the four atoms (N1, O1, C1, C7) occupy the tetrahedral sites (Fig. 2). All bond distances and bond angles are chemically reasonable. For example, the average P-O bond distance of 1.489(2)Å is typical of a P-O double bond.<sup>8</sup>

All three NH hydrogen atoms are involved in hydrogen bonds of the type N-H...O. There are two intramolecular and one intermolecular hydrogen bonds (Table 4). The two intramolecular hydrogen bonds link three molecules of compound 1 to generate a trimeric structure. The intermolecular hydrogen bond participates in the crystal packing.

In summary, we have isolated diphenyl(*tert*-butylamino) phosphine oxide, O=PPh<sub>2</sub>(NH-*t*-Bu), (1) from RhCl(PPh<sub>3</sub>)<sub>3</sub> and LiNH-*t*-Bu. The structure of compound 1 shows that three molecules are linked through N-H...O hydrogen bonding to form a trimeric structure.

## SUPPLEMENTARY MATERIAL

Tables of full bond distances and bond angles, aniso-

tropic thermal parameters for non-hydrogen atoms, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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