

# Synthesis and Structure of $[\text{Ni}(\text{dppe})_2]$ ( $\text{dppe}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ )

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## $[\text{Ni}(\text{dppe})_2]$ 의 합성 및 구조

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### Abstract

Compound  $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$  (**1**) reacted with bis(diphenylphosphino)ethane ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Ph}_2$ , dppe) to give bis(bis(diphenylphosphino)ethane)nickel(0),  $[\text{Ni}(\text{dppe})_2]$  (**2**). Compound **2** was characterized by spectroscopy ( $^1\text{H}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR) and X-ray crystallography. Crystallographic data for **2**: monoclinic space group  $P2_1/n$ ,  $a=9.826(1)$  Å,  $b=21.167(2)$  Å,  $c=21.425(2)$  Å,  $\beta=91.957(9)^\circ$ ,  $Z=4$ ,  $R(wR_2)=0.0377(0.0882)$ .

### 1. Introduction

Zerovalent nickel complexes of tertiary phosphines ( $\text{PR}_3$ ) and tertiary phosphites ( $\text{P}(\text{OR})_3$ ) have been extensively studied because of their important roles in organic synthesis.<sup>1,2)</sup> For example, they have proved to be quite active as polymerization catalysts for acetylenic compounds.<sup>3)</sup>

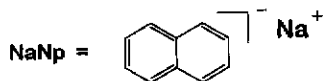
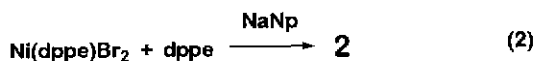
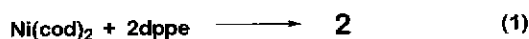
The title compound,  $[\text{Ni}(\text{dppe})_2]$  (**2**), was previously prepared from bis(1,5-cyclooctadiene)nickel(0),  $[\text{Ni}(\text{cod})_2]$ , and bis(diphenylphosphino)ethane (dppe) in hexane (eq. 1)<sup>4)</sup> or by the reduction of  $[\text{Ni}(\text{dppe})\text{Br}_2]$  with sodium naphthalenide ( $\text{Na}[\text{C}_{10}\text{H}_8]$ ,  $\text{NaNp}$ ) in the presence of the free dppe in tetrahydrofuran (eq. 2).<sup>5)</sup> However, the X-ray structure of the title compound has not been reported yet. We prepared the title compound in a different way. When we treated tetrakis

(triethyl phosphite)nickel(0),  $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$  (**1**), with dppe, the title compound was obtained. We report here the preparation and structure of  $[\text{Ni}(\text{dppe})_2]$  (**2**).

### 2. Experimental Section

Unless otherwise stated, all the 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- or oven-dried. Diethyl ether ( $\text{Et}_2\text{O}$ ) was distilled over sodium metal under argon. The NMR solvent ( $\text{CDCl}_3$ ) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Bis(diphenylphosphino)ethane ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Ph}_2$ , dppe) was purchased from Fluka company. Compound  $[\text{Ni}(\text{P}(\text{OEt})_3)_4]$  (**1**) was prepared by the literature method.<sup>6)</sup>

$^1\text{H}$ - spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane.  $^{31}\text{P}\{^1\text{H}\}$ -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>. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration.

**Preparation of [Ni(dppe)<sub>2</sub>] (2).** At room temperature, 0.39 g (1.00 mmol) of dppe in 10 mL of Et<sub>2</sub>O was added to 0.40 g (0.56 mmol) of compound **1** in 30 mL of Et<sub>2</sub>O. The resulting solution was stirred for 3 days, during which its color turned from colorless to yellow-orange. The solution was filtered, and solvent was removed under vacuum. The resulting yellow residue was washed with hexane (20 mL×3) to give orange solid (0.19 g, 42%), which was recrystallized from dichloromethanehexane to give crystals of [Ni(dppe)<sub>2</sub>] (**2**).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.995-6.968 (40H, m, Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>), 2.084 (4H, broad, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ 44.875. mp: 253-255°C.

**X-ray Structure Determination.** All X-ray data were collected with 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 22 reflections in the range 15.0<2θ<25.0°. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with y-scan data. All calculations were carried out with use of the SHELXTL programs.<sup>71</sup>

An orange crystal of **2** of approximate dimensions 0.62×0.40×0.36 mm<sup>3</sup>, shaped as a block, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*0*l* (*h*+*l*=2*n*+1) and 0*k*0 (*k*=2*n*+1), unambiguously indicated *P*2<sub>1</sub>/*n* as a space group. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model.

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

**Table 1. X-ray data collection and structure refinement**

formula	C <sub>32</sub> H <sub>48</sub> P <sub>4</sub> Ni
fw	855.49
temperature, K	295(2)
crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	9.826(1)
<i>b</i> , Å	21.167(2)
<i>c</i> , Å	21.425(2)
β, deg	91.957(9)
<i>V</i> , Å <sup>3</sup>	4453.5(8)
<i>Z</i>	4
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.276
μ, mm <sup>-1</sup>	0.614
<i>T</i> <sub>min</sub>	0.4655
<i>T</i> <sub>max</sub>	0.8260
<i>F</i> (000)	1792
<i>R</i> (int)	0.0348
No. of reflections measured	8672
No. of reflections unique	8173
No. of reflections with <i>I</i> >2σ( <i>I</i> )	6354
No. of parameters refined	515
2θ range (°)	3.5-51.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on <i>F</i> <sup>2</sup> )	1.010
Max., min. in Δρ (e Å <sup>-3</sup> )	0.331, -0.289
<i>R</i>	0.0377
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.0882

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

in Tables 2 and 3, respectively.

### 3. Results and Discussion

**Preparation.** A Ni(0)-bis(diphosphine) complex, [Ni(dppe)<sub>2</sub>] (**2**), has been prepared by the substitution of the P(OEt)<sub>3</sub> ligands in [Ni(P(OEt)<sub>3</sub>)<sub>4</sub>] (**1**) by chelating diphosphine dppe (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>Ph<sub>2</sub>) (**1**) in diethyl ether (eq. 3). During the reaction, an initially colorless solution turned to a yellow-orange solution. The solid product was recrystallized from dichloromethanehexane to give X-ray quality crystals. There has been no change in the formal oxidation number of the nickel metal.

**Structure.** The structure of **2** with the atomic

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

	x	y	z	$U(\text{eq})^a$
Ni(1)	1328(1)	7991(1)	2325(1)	33(1)
P(1)	-224(1)	7311(1)	2033(1)	39(1)
P(2)	-80(1)	8755(1)	2130(1)	38(1)
P(3)	2446(1)	8071(1)	3212(1)	41(1)
P(4)	3194(1)	8061(1)	1828(1)	42(1)
C(1)	-1782(3)	7780(1)	1835(1)	56(1)
C(2)	-1375(3)	8422(1)	1583(1)	52(1)
C(3)	4284(3)	8044(1)	3027(1)	58(1)
C(4)	4509(3)	8354(2)	2396(1)	60(1)
C(5)	-889(3)	6692(2)	2543(1)	58(1)
C(6)	-56(5)	6179(2)	2661(2)	102(1)
C(7)	-450(7)	5702(2)	3063(3)	144(2)
C(8)	-1676(9)	5734(3)	3334(3)	153(3)
C(9)	-2482(7)	6215(4)	3221(3)	153(3)
C(10)	-2100(4)	6701(2)	2827(2)	106(1)
C(11)	-121(2)	6832(1)	1312(1)	42(1)
C(12)	-1163(3)	6420(1)	1128(1)	59(1)
C(13)	-1104(4)	6083(2)	580(2)	72(1)
C(14)	-9(4)	6149(2)	209(2)	75(1)
C(15)	1032(4)	6542(2)	387(1)	76(1)
C(16)	969(3)	6884(1)	934(1)	57(1)
C(17)	-1194(2)	9027(1)	2752(1)	45(1)
C(18)	-1459(3)	8620(1)	3234(1)	57(1)
C(19)	-2325(3)	8792(2)	3708(2)	78(1)
C(20)	-2906(4)	9378(2)	3701(2)	90(1)
C(21)	-2666(4)	9784(2)	3227(2)	94(1)
C(22)	-1809(3)	9615(2)	2756(2)	70(1)
C(23)	369(3)	9507(1)	1772(1)	52(1)
C(24)	-62(4)	9699(2)	1180(2)	81(1)
C(25)	368(6)	10274(2)	942(2)	112(2)

**Table 2. Continued**

	x	y	z	$U(\text{eq})^a$
C(26)	1194(6)	10662(2)	1282(3)	122(2)
C(27)	1613(5)	10482(2)	1860(3)	110(2)
C(28)	1224(4)	9905(2)	2102(2)	80(1)
C(29)	2372(3)	7522(1)	3876(1)	49(1)
C(30)	1266(3)	7133(2)	3926(1)	65(1)
C(31)	1133(4)	6739(2)	4438(2)	80(1)
C(32)	2138(4)	6730(2)	4898(1)	81(1)
C(33)	3238(5)	7112(2)	4853(2)	93(1)
C(34)	3364(4)	7503(2)	4348(1)	76(1)
C(35)	2355(3)	8821(1)	3654(1)	48(1)
C(36)	3203(3)	9325(1)	3562(1)	65(1)
C(37)	3048(4)	9891(2)	3879(2)	79(1)
C(38)	2030(4)	9957(2)	4292(2)	78(1)
C(39)	1172(4)	9466(2)	4391(2)	78(1)
C(40)	1327(3)	8900(1)	4081(1)	62(1)
C(41)	3308(3)	8607(1)	1164(1)	57(1)
C(42)	4169(5)	9114(2)	1146(2)	110(2)
C(43)	4100(7)	9530(2)	633(2)	143(2)
C(44)	3228(6)	9428(2)	146(2)	124(2)
C(45)	2412(5)	8915(2)	146(2)	107(1)
C(46)	2426(4)	8522(2)	662(2)	90(1)
C(47)	4069(2)	7359(1)	1528(1)	48(1)
C(48)	4001(3)	6803(1)	1863(2)	64(1)
C(49)	4615(4)	6252(2)	1658(2)	77(1)
C(50)	5270(3)	6252(2)	1110(2)	78(1)
C(51)	5354(3)	6794(2)	769(2)	74(1)
C(52)	4768(3)	7347(2)	977(1)	59(1)

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

**Table 3. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )**

Ni1-P1	2.1733(7)	Ni1-P2	2.1583(7)	Ni1-P3	2.1689(7)
Ni1-P4	2.1564(7)	P1-C1	1.861(3)	P1-C5	1.840(3)
P1-C11	1.855(2)	P2-C2	1.842(3)	P2-C17	1.845(2)
P2-C23	1.830(3)	P3-C3	1.862(3)	P3-C29	1.839(3)
P3-C35	1.852(2)	P4-C4	1.851(3)	P4-C41	1.839(3)
P4-C47	1.844(3)	C1-C2	1.521(4)	C3-C4	1.526(4)
P4-Ni1-P2	113.77(3)	P4-Ni1-P3	90.77(3)	P2-Ni1-P3	114.40(3)
P4-Ni1-P1	120.23(3)	P2-Ni1-P1	90.07(3)	P3-Ni1-P1	129.30(3)
C5-P1-C11	97.8(1)	C5-P1-C1	102.1(1)	C11-P1-C1	99.7(1)
C5-P1-Ni1	124.14(9)	C11-P1-Ni1	122.98(8)	C1-P1-Ni1	106.06(9)
C23-P2-C2	103.7(1)	C23-P2-C17	100.9(1)	C2-P2-C17	99.5(1)
C23-P2-Ni1	124.85(9)	C2-P2-Ni1	105.15(9)	C17-P2-Ni1	119.10(8)
C29-P3-C35	98.2(1)	C29-P3-C3	102.1(1)	C35-P3-C3	101.5(1)
C29-P3-Ni1	126.55(9)	C35-P3-Ni1	118.90(8)	C3-P3-Ni1	106.07(9)
C41-P4-C47	101.2(1)	C41-P4-C4	103.9(1)	C47-P4-C4	100.1(1)
C41-P4-Ni1	120.05(9)	C47-P4-Ni1	122.10(8)	C4-P4-Ni1	106.55(9)

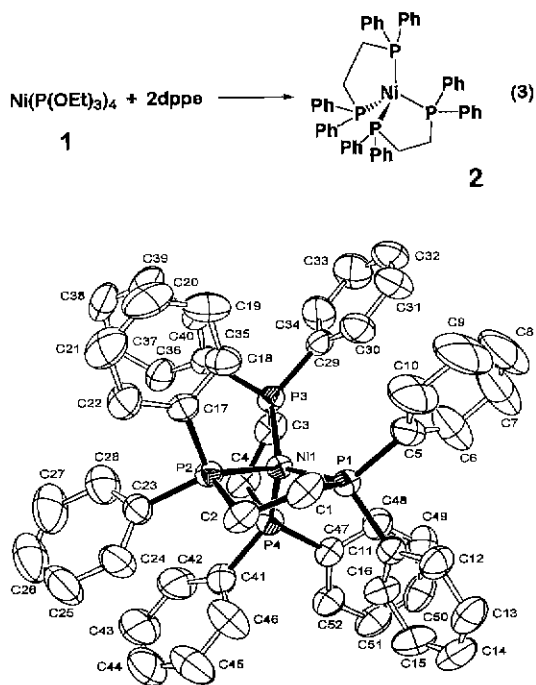


Fig. 1. ORTEP drawing of 2 with the atom-labeling scheme and 50% probability thermal ellipsoids.

numbering scheme is shown in Fig. 1. The coordination sphere of Ni can be described as a tetrahedron, in which the four phosphorus atoms of the dppe ligands occupy the tetrahedral sites. The triangular plane of Ni1, P1 and P2 is essentially perpendicular to that of Ni1, P3, and P4, with a dihedral angle of 87.29°.

As shown in Fig. 1, the molecule is pretty bulky. All bond distances and bond angles are normal within experimental error. Compound 2 appears to have a tetrahedral symmetry that might account for the singlet for the four phosphorus nuclei in its <sup>31</sup>P{<sup>1</sup>H}-NMR spectra. The results of the X-ray

structure and NMR spectral data indicate that this compound has the same structure both in solution and in the solid state.

In summary, we have prepared the bis(diphosphine) Ni(0) complex, [Ni(dppe)<sub>2</sub>] (2), by treating [Ni(P(OEt)<sub>3</sub>)<sub>4</sub>] (1) with dppe. The molecular structure of compound 2 shows that the molecule is very crowded around the central Ni metal and has a tetrahedral geometry.

#### 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

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