Capped Trigonal Prismatic Yttrium Complex with Mixed Tri- and Bi-dentate Ligands: Synthesis and X-ray Crystal Structure of Bis[dihydrobis(pyrazol-1-yl)borato]-[(η^5-Cp)tris(dimethylphosphito-*P*)cobalt-*O,O',O''*]yttrium

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The anionic cobalt(III)-based oxygen tripod ligand, L_{OR} (L_{OR} = [CpCo{P(=O)(OR)$_2$}$_3$]$^-$), as an oxygen analog for cyclopentadienyl or hydrotris(pyrazol-1-yl)borate has been introduced by Kläui and coworkers.[1] Various transition metal complexes with the ligands have been prepared due to their high stabilities and π-donation abilities.[2] However, the studies of early transition metal complexes containing the ligands are rare.[3] In 1992, Nolan and co-workers[4] have reported a dimeric yttrium complex containing L_{OEt} resulted from Arbuzov dealkylation of $(L_{OEt})_2$YCl at elevated temperature. Recently, a dimeric zirconium complex with L_{OMe} ligands afforded from $(L_{OMe})_2ZrCl_2$ by double Arbuzov dealkylation has also been reported.[5]

Our recent studies on the formation of yttrium complexes containing L_{OMe} ligands, $(L_{OMe})_2$(acetato)Y, revealed that the acetato ligand is bound to yttrium as an isobidentate fashion due to the bulkiness of L_{OMe}.[6] Additionally, $(L_{OMe})_2$(acetylacetonato)Y, which is containing a bulkier ligand than the acetato complex, has been isolated and fully characterized.[7] Herein, we wish to report a monocapped trigonal prismatic yttrium complex, containing one L_{OMe} and two dihydrobis(pyrazol-1-ly)borato, [H$_2$B(pz)$_2$]$^-$, ligands.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an argon atmosphere. All solvents were dried and deoxygenated over sodium/benzophenone ketyl, and distilled under argon immediately prior to use. $CDCl_3$ and CD_2Cl_2 (Aldrich Co.) were dried over activated 4 molecular sieves. YCl_3 (Aldrich Co. 99.99%) was used as received. NaL_{OMe} and KH$_2$B(pz)$_2$ were prepared according to the previous mothods.[1,8] FT-IR spectrum was recorded on a Bomen Michelson 100 spectrophotometer as a KBr pellet. All ^{1}H NMR spectra were obtained on a Varian Gemini-200 spectrometer. A mixed solvent ($CDCl_3/CD_2Cl_2$ = 1.5) was used for obtaining ^{1}H NMR spectra at low temperatures down to -115 °C. Chemical analyses were carried out by the Chemical Analysis Laboratory at Korea Basic Science Institute.

Synthesis. 50 mL of THF was introduced to a mixture of YCl_3 (0.136 g, 0.001 mol), NaL_{OMe} (0.476 mg, 0.001 mol), and KH$_2$B(pz)$_2$ (0.373 g, 0.002 mol). White precipitates were formed after stirring the reaction mixture for 2 days at room temperature. The precipitate was filtered off to afford a yellow solution. The solution was concentrated and cooled to give yellow crystals (0.583 g, 70% yield based on YCl_3).

Anal. Calcd. for $C_{23}H_{39}B_2N_8O_9P_3CoY$: C, 33.12; H, 4.71; N, 13.43. Found: C, 33.36; H, 4.87; N, 13.21. IR (KBr Pellet): 2990 (w), 2946 (m), 2839 (w), 2414 (br, m), 1501 (w), 1403 (m), 1300 (m), 1127 (s), 1052 (s), 1013 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.46 and 7.13 (4, 4; d, d; J = 1.46, 1.68 Hz; 3-H, 5-H (pyrazolyl)), 6.01 (4, t, J = 1.98 Hz; 4-H (pyrazolyl)), 5.11 (5, broad s, Cp), 3.62 (18, m, H$_3$C-O-P).

X-ray Structure Analysis. A yellow single crystal (tetragonal rod, 0.50×0.40×0.40 mm) was sealed in a thin walled glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters and orientation matrix for data collection were determined by least-squares refinement using 25 reflections in the range of 18° < 2θ < 30°. A total of 3986 reflections were collected in the 2θ range of 2.94-53° ($-11 \le h \le 0$, $0 \le k \le 23$, $0 \le l \le 24$) at room temperature using ω-2θ scan mode, of which 2786 with $I > 2\sigma(I)$ were used in the refinement of the structure. Three standard reflections were monitored every one hour during data collection, which was indicating no significant intensity decay. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scans was applied to the data (correction coefficients, 0.7263 to 0.9996).[9]

The structure was determined by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXS-97[10] and SHELXL-97.[11] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were calculated geometrically using a riding model with 1.2 times isotropic thermal factors of the attached non-hydrogen atoms except hydrogen atoms on methyl groups which were located using the same method with 1.5 times thermal parameters of methyl carbon atoms. The final cycle of the refinement converged to error indices of R = 0.045 and wR = 0.071. The maximum remaining electron density was 0.34 e/Å^3 at 1.41 Å from P(1). No parameter shifted more than 0.1% of its estimated standard deviation during the last least-squares refinement. The data processing and refinement parameters are listed in Table 1. Selected bond distances and angles are presented in Table 2.

Results and Discussion

Preparation of the compound is realized by the stoichio-

Table 1. Crystal Data and Structure Refinement for $(L_{OMe})Y[H_2B(pz)_2]_2$

Empirical formula	$C_{23}H_{30}B_2CoN_8O_9P_3Y$
Formula weight	833.99
Temperature	293(2) K
Space group	$P2_12_12_1$
Unit cell dimensions	a = 9.455(2) Å
	b = 19.137(5) Å
	c = 20.099(5) Å
Volume	3632(2) Å^3
Z, Calculated density	4, 1.523 Mg m^{-3}
Absorption coefficient	2.232 mm^{-1}
F(000)	1704
Refinement method	Full-matrix least-squares on F^2
Data / parameters	2786 / 424
Goodness-of-fit on F^2	1.071
Final R indices [I > 2σ(I)]	R = 0.045, wR = 0.071

$R = \Sigma \| F_o|-|F_c\| / \Sigma F_o$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{1/2}$

Table 2. Bond lengths [Å] and Angles [°] for $(L_{OMe})Y[H_2B(pz)_2]_2$

Y-O(1)	2.253(5)	Y-O(2)	2.236(5)
Y-O(3)	2.329(5)	Y-N(1)	2.422(7)
Y-N(3)	2.444(6)	Y-N(5)	2.489(7)
Y-N(7)	2.508(7)	Co-P(1)	2.162(3)
Co-P(2)	2.167(3)	Co-P(3)	2.171(3)
P(1)-O(1)	1.506(6)	P(2)-O(2)	1.511(5)
P(3)-O(3)	1.503(6)	P(1)-O(5)	1.574(7)
P(1)-O(4)	1.603(7)	P(2)-O(7)	1.591(6)
P(2)-O(6)	1.598(6)	P(3)-O(9)	1.585(6)
P(3)-O(8)	1.605(7)	N(2)-B(1)	1.54(1)
N(4)-B(1)	1.54(1)	N(6)-B(2)	1.55(1)
N(8)-B(2)	1.52(1)		
O(2)-Y-O(1)	83.7(2)	O(1)-Y-N(5)	83.8(2)
O(2)-Y-O(3)	78.3(2)	O(3)-Y-N(5)	142.0(2)
O(1)-Y-O(3)	77.1(2)	N(1)-Y-N(5)	119.4(2)
O(2)-Y-N(1)	88.7(2)	N(3)-Y-N(5)	75.1(2)
O(1)-Y-N(1)	153.2(2)	O(2)-Y-N(7)	77.0(2)
O(3)-Y-N(1)	76.3(2)	O(1)-Y-N(7)	125.4(2)
O(2)-Y-N(3)	152.5(2)	O(3)-Y-N(7)	143.8(2)
O(1)-Y-N(3)	97.5(2)	N(1)-Y-N(7)	77.1(3)
O(3)-Y-N(3)	75.3(2)	N(3)-Y-N(7)	122.0(3)
N(1)-Y-N(3)	77.9(2)	N(5)-Y-N(7)	73.4(2)
O(2)-Y-N(5)	132.2(2)		

metric mixture of YCl_3 and the ligand salts in THF solvent.

$$YCl_3 + NaL_{OMe} + 2\ KH_2B(pz)_2 \rightarrow (L_{OMe})Y[H_2B(pz)_2]_2 + NaCl + 2\ KCl$$

The ^{1}H NMR spectrum of the compound at ambient temperature displayed two doublets at δ 7.46 and δ 7.13 and a triplet at 6.01, corresponding to the aromatic protons of the pyrazolyl rings (*vide infra*). A broad single resonance at δ 5.11 was assigned to the protons of the Cp ring. The protons of methoxy groups attached to phosphorus atoms were observed at δ 3.62 as a multiplet. The intensity ratio of the observed peaks indicates that the compound contains one

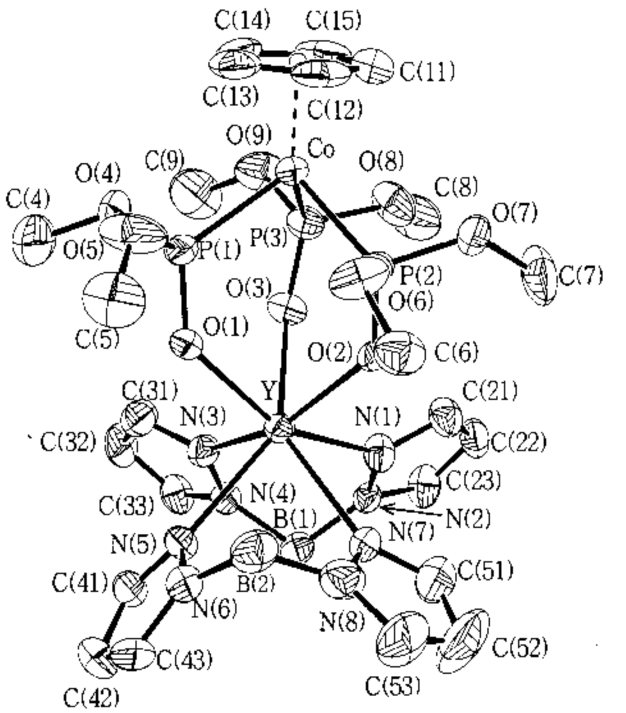

Figure 1. ORTEX diagram of $(L_{OMe})Y[H_2B(pz)_2]_2$ (the ellipsoids correspond to 40% probability). Hydrogen atoms are omitted for clarity.

L_{OMe} and two $[H_2B(pz)_2]^-$ ligands. In order to illustrate the molecular structure of the compound, an X-ray crystal structure has been determined. An ORTEX drawing[12] with atomic labeling scheme of the compound is shown in Figure 1. The coordination geometry around Y atom shown in Figure 2 is nearly a mono-capped trigonal prism contributed from O(1), O(2), O(3) *via* L_{OMe} and N(1), N(3), N(5), N(7) from two $[H_2B(pz)_2]^-$ ligands. O(1), O(2), N(7), and N(5) are nearly co-planar within deviations of less than 0.081(3) Å and N(1), N(3), N(5), N(7) are almost planar with no devia-

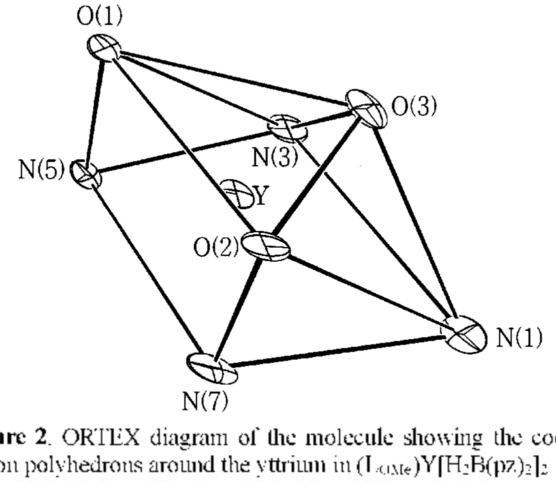

Figure 2. ORTEX diagram of the molecule showing the coordination polyhedrons around the yttrium in $(L_{OMe})Y[H_2B(pz)_2]_2$

O(1)-N(3)-N(5)	57.4(2)	N(3)-N(1)-N(7)	89.8(3)
O(1)-N(5)-N(3)	69.7(2)	N(1)-N(3)-N(5)	88.8(3)
O(2)-N(1)-N(7)	55.7(2)	N(3)-N(5)-N(7)	92.6(3)
O(2)-N(7)-N(1)	65.3(2)	N(5)-N(7)-N(1)	88.8(3)
O(2)-N(7)-N(5)	93.1(3)	O(2)-N(1)-N(3)	92.0(2)
N(7)-N(5)-O(1)	86.8(2)	N(1)-N(3)-O(1)	86.9(2)

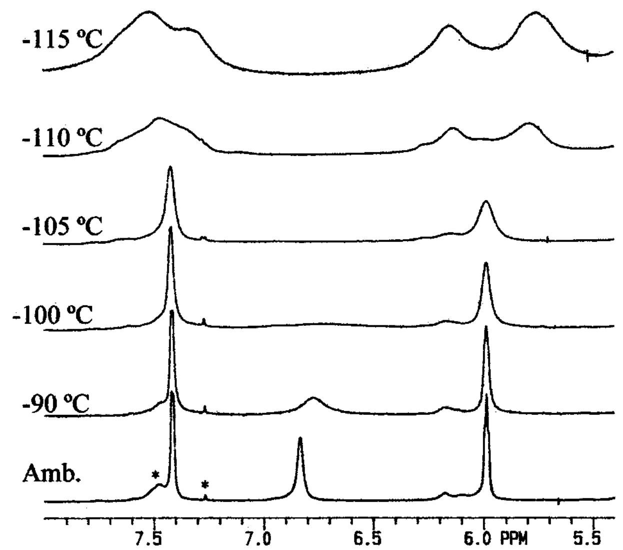

Figure 3. Variable-temperature ^{1}H NMR spectra of $(L_{OMe})Y[H_2B(pz)_2]_2$ covering the pyrazolyl region. (*) indicates the signals for the impurities.

tions of more than 0.021(4) Å and O(1), O(2), N(1), N(3) are in the same plane with displacements of less than 0.004(3) Å, that contains O(3) as capped atom. The angle between trigonal planes [O(1), N(3), N(5) and O(2), N(1), N(7)] is 1.5(3)°, indicating nearly parallel. Y-O(1) and Y-O(2) separations are similarly 2.253(5) and 2.236(5) Å. Y-O(3) distance is 2.329(5) Å, which is somewhat longer than those of Y-O(1) and Y-O(2). Distances of Y-N(1) and Y-N(3) from a $[H_2B(pz)_2]$- ligand are 2.422(7) and 2.444(6) Å, which are a little longer than those in $[H(\mu\text{-H})B(pz)_2]_3Y$ [mean of Y-N bond distances is 2.390(6) Å][13] due to the influence of the bulk L_{OMe} ligand. Bond distances of Y-N(5) and Y-N(7) from another $[H_2B(pz)_2]$ ligand are 2.489(7) and 2.508(7) Å, which are somewhat longer than those of Y-N(1) and Y-N(3). Therefore, two $[H_2B(pz)_2]$ ligands are non-equivalent in the solid state.

However, the ^{1}H NMR spectrum of the compound in $CDCl_3$ at ambient temperature shows only three resonances corresponding to the 5-, 3-, and 4- protons (5-H indicates proton at near B atom), of all equivalent pyrazolyl rings (*vide supra*), implying that there is a dynamic process in solution. Thus, further VT-NMR experiments at low temperatures down to -115 °C were performed using a mixed solvent ($CDCl_3/CD_2Cl_2$ = 1.5), of which results is shown in Figure 3. Down to -80 °C, the resonances for 5-, 3-, and 4-protons of pyrazolyl rings were similarly observed to those at ambient temperature. Just below this temperature, the doublet resonances for 3-protons of the pyrazolyl rings suddenly collapsed and broadened, indicating that a structural environment in the complex was greatly influenced by the difference of bond distances between yttrium and nitrogen atoms of the pyrazolyl rings or by the change of coordination environment around yttrium atom. At -100 °C all the signals entirely collapsed, resulting in the disappearance of the signals of the 3-protons, while the other two resonances for 5- and 4-protons remained as broad. At -115 °C two additional broad resonances appeared at δ 6.2 and δ 7.3, indicating that the two sets of 3-protons in the pyrazolyl rings, which seem to be most sensitive to the change of the structural environment in the complex, starts to resolve while the resonances for 5- and 4-protons of pyrazolyl rings broadened and shifted. However, the signals of pyrazolyl protons of the frozen structure in solution could not observed in the ^{1}H NMR spectrum due to the limitation of solvent freezing. Therefore, explanation for the dynamic process illustrated unclearly with the obtainable data.

Consequently, a seven coordinate yttrium complex containing one L_{OMe} and two $[H_2B(pz)_2]$ ligands has been isolated and fully characterized. The coordination environment around yttrium atom is a distorted mono-capped trigonal prism. The two $[H_2B(pz)_2]$ ligands in the complex were in dynamic processes down to -115 °C in solution.

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Supplementary Material Available. Tables of detailed crystallographic data, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, bond distances and angles, anisotropic displacement parameters, hydrogen coordinate and isotropic displacement parameters are available from JJH (Tel. 82-53-950-6343; Fax. 82-53-950-6330; email: jeongjh@kyungpook.ac.kr).

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