

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

Sang Ho Han, Soonheum Park,[†] and Jong Hwa Jeong*

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

[†]Department of Chemistry, Dongguk University, Kyong-Ju 780-714, Korea

Received March 9, 1999

The anionic cobalt(III)-based oxygen tripod ligand, L_{OR} (L_{OR} = [CpCo{P(=O)(OR)₂}]⁻), 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-workers⁴ have reported a dimeric yttrium complex containing L_{OEt} resulted from Arbuzov dealkylation of (L_{OEt})₂YCl at elevated temperature. Recently, a dimeric zirconium complex with L_{OMe} ligands afforded from (L_{OMe})₂ZrCl₂ 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-yl)borato, [H₂B(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. CDCl₃ and CD₂Cl₂ (Aldrich Co.) were dried over activated 4 molecular sieves. YCl₃ (Aldrich Co. 99.99%) was used as received. NaL_{OMe} and KH₂B(pz)₂ were prepared according to the previous methods.^{1,8} FT-IR spectrum was recorded on a Bomen Michelson 100 spectrophotometer as a KBr pellet. All ¹H NMR spectra were obtained on a Varian Gemini-200 spectrometer. A mixed solvent (CDCl₃/CD₂Cl₂ = 1.5) was used for obtaining ¹H 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 YCl₃ (0.136 g, 0.001 mol), NaL_{OMe} (0.476 mg, 0.001 mol), and KH₂B(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 YCl₃).

Anal. Calcd. for C₂₃H₃₉B₂N₈O₉P₃CoY: 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. ¹H NMR (CDCl₃): 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, H₃C-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 K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters and orientation matrix for data collection were determined by least-squares refinement using 25 reflections in the range of $18^\circ < 2\theta < 30^\circ$. A total of 3986 reflections were collected in the 2θ range of 2.94 – 53° ($-11 \leq h \leq 0$, $0 \leq k \leq 23$, $0 \leq l \leq 24$) 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 F² using SHELXS-97¹⁰ 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/Å³ 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-[H₂B(pz)₂]₂

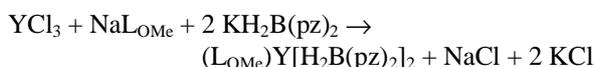
Empirical formula	C ₂₃ H ₃₉ B ₂ CoN ₈ O ₉ P ₃ Y
Formula weight	833.99
Temperature	293(2) K
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 9.455(2) Å b = 19.137(5) Å c = 20.099(5) Å
Volume	3632(2) Å ³
Z, Calculated density	4, 1.523 Mg/m ³
Absorption coefficient	2.232 mm ⁻¹
F(000)	1704
Refinement method	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

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

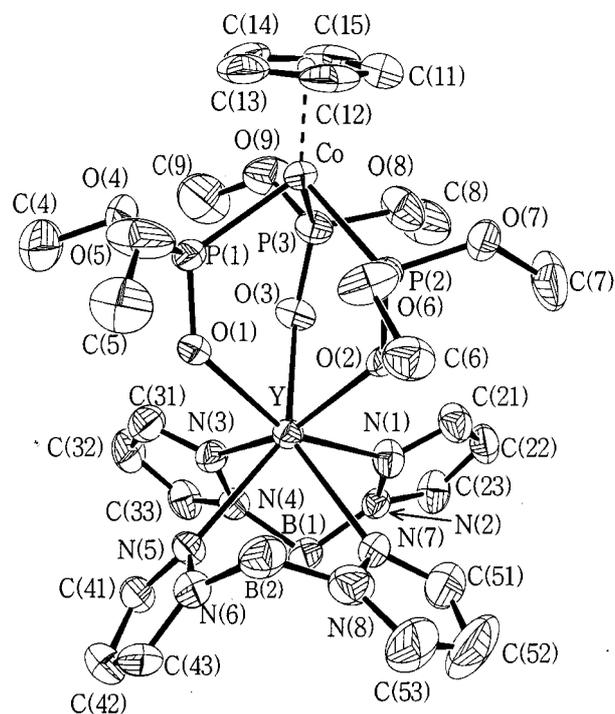
Table 2. Bond lengths [Å] and Angles [°] for (L_{OMe})Y[H₂B(pz)₂]₂

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)		

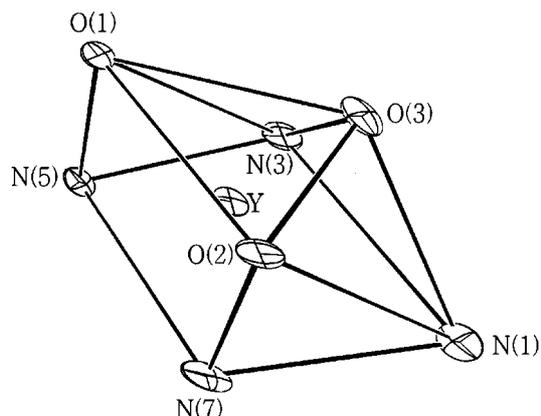
metric mixture of YCl₃ and the ligand salts in THF solvent.



The ¹H 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[H₂B(pz)₂]₂ (the ellipsoids correspond to 40% probability). Hydrogen atoms are omitted for clarity.

L_{OMe} and two [H₂B(pz)₂]⁻ ligands. In order to illustrate the molecular structure of the compound, an X-ray crystal structure has been determined. An ORTEX drawing¹² 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 [H₂B(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[H₂B(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)

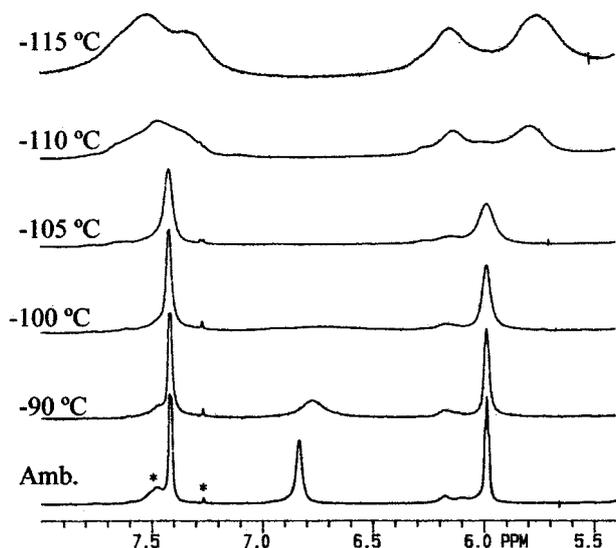


Figure 3. Variable-temperature ^1H NMR spectra of $(\text{LOMe})\text{Y}[\text{H}_2\text{B}(\text{pz})_2]_2$ covering the pyrazolyl region. (*) indicates the signals for the impurities.

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 $1.5(3)^\circ$, 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 $[\text{H}_2\text{B}(\text{pz})_2]^-$ ligand are $2.422(7)$ and $2.444(6)$ Å, which are a little longer than those in $[\text{H}(\mu\text{-H})\text{B}(\text{pz})_2]_3\text{Y}$ [mean of Y-N bond distances is $2.390(6)$ Å]¹³ due to the influence of the bulk LOMe ligand. Bond distances of Y-N(5) and Y-N(7) from another $[\text{H}_2\text{B}(\text{pz})_2]^-$ 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 $[\text{H}_2\text{B}(\text{pz})_2]^-$ ligands are non-equivalent in the solid state.

However, the ^1H 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 ($\text{CDCl}_3/\text{CD}_2\text{Cl}_2 = 1.5$), 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 be observed in the ^1H 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 LOMe and two $[\text{H}_2\text{B}(\text{pz})_2]^-$ ligands has been isolated and fully characterized. The coordination environment around yttrium atom is a distorted mono-capped trigonal prism. The two $[\text{H}_2\text{B}(\text{pz})_2]^-$ ligands in the complex were in dynamic processes down to -115 °C in solution.

Acknowledgment. This research has been supported financially by the Korea Science and Engineering Foundation and Basic Science Research Institute Program of Ministry of Education in Korea.

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).

References

1. Kläui, W. *Z. Naturforsch.* **1979**, *34B*, 1403-1407.
2. Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627-637.
3. Kläui, W.; Müller, A.; Eberspach, W.; Boese, R.; Goldber, I. *J. Am. Chem. Soc.* **1987**, *109*, 164-169.
4. Liang, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1992**, *11*, 3459-3462.
5. Cho, I. Y.; Yeo, H. J.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1995**, *16*, 1244-1246.
6. Kim, N. H.; Yeo, H. J.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1996**, *17*, 483-485.
7. Kim, K.-C.; Park, Y.-C.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1997**, *18*, 670-672.
8. Trofemenko, S. *Inorg. Synth.* **1970**, *12*, 100-101.
9. Fair, C. K. *Molen: An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands, 1990.
10. Sheldrick, G. M. *SHELXS-97: Program for the solution of crystal structures*; Univ. of Göttingen: Germany, 1990.
11. Sheldrick, G. M. *SHELXL-97: Programs for crystal structure refinement*; Univ. of Göttingen: Germany, 1997.
12. McArdle, P. J. *Appl. Cryst.* **1995**, *28*, 65-65.
13. Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1890-1896.