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Preparation and Characterization of $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$

Sang-hyuk Lee, Hwan Jin Yeo*, and Jong Hwa Jeong*

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

Received November 15, 1995

Transition metal complexes containing $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ have been widely studied.^{1,2} But yttrium complexes of the ligand are not known. The coordination chemistry of yttrium has become considerable attraction since yttrium complexes reveal the catalytic activities for ring-opening polymerization³ or α -olefin polymerization.⁴ The common coordinate number of yttrium is seven or eight because of relatively large ionic radius⁵ and six coordinate complexes which are structurally well defined are very rare.^{6,7} We here report the crystal structure for a six-coordinate, homoleptic complex of yttrium.

Experimental

All manipulations were performed under an argon atmosphere using a double manifold vacuum system and Schlenk techniques at room temperature. Solvents were purified by standard methods and were freshly dried and distilled prior to use. YCl_3 was purchased from Aldrich Co. and used as received. $\text{H}_4\text{N}[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ was prepared by the literature method.¹

¹H NMR spectrum was obtained in C_6D_6 and referenced to internal deuterated solvent and recalculated relative to TMS on a Bruker AM-300 spectrometer. Chemical analyses were carried out by the Chemical Analysis Laboratory at KBSC.

Preparation of $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$. To a mixture of 1.5 mmol of $\text{H}_4\text{N}[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ and 0.5 mmol of YCl_3 , 20 mL of dry THF was introduced. The resulting suspension was stirred at room temperature for 24 h and then the precipitate was filtered off. The filtrate

Table 1. Crystal data and structure refinement for $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]_3\text{Y}$

Empirical formula	$\text{C}_{27} \text{H}_{51} \text{Ni}_3 \text{O}_{18} \text{P}_6 \text{Y}$
Formula weight	1114.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a = 18.428(2)$ Å $b = 11.535(2)$ Å $c = 21.793(2)$ Å $\beta = 107.213(9)^\circ$
Volume	4424.9(1) Å ³
Z	4
Density (calculated)	1.673 Mg/m ³
Absorption coefficient	2.838 mm ⁻¹
F(000)	2280
Absorpt.-correction T min	0.866
Absorpt.-correction T max	1.000
Crystal size	0.50 × 0.50 × 0.35 mm
Theta range for data collection	2.84 to 26.29°
Index ranges	$0 \leq h \leq 22$, $-14 \leq k \leq 0$, $-27 \leq l \leq 25$
Reflections collected	6379
Independent reflections	6181 [R(int)=0.0187]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6179/0/407
Goodness-of-fit on F ²	1.038
Final R indices [I > 2σ(I)]	$R_1 = 0.0542$, $wR_2 = 0.1206$
R indices (all data)	$R_1 = 0.0595$, $wR_2 = 0.1253$
Largest diff. peak and hole	0.953 and -0.923 e.Å ⁻³

was evaporated *in vacuo* to give reddish brown solid. Recrystallization of the crude product from a solvent pair of toluene-hexane affords reddish brown crystals in 85% yield.

Analysis: Calcd. (%) C; 29.14, H; 4.61 Found (%) C; 29.04, H; 4.56.

¹H NMR (C_6D_6): δ 5.35 (s, C_5H_5 , 5H), δ 3.58 (m, $(\text{H}_3\text{CO})\text{P}(\text{O})_2$, 6H)

X-ray crystallographic analysis. A X-ray quality single crystal, 0.50 × 0.50 × 0.35 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å), unit cell parameters were determined by least-squares analysis of 25 reflections ($10^\circ < \theta < 13^\circ$). Intensity data were collected with θ range of 2.84-26.29° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 hr during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with Ψ scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on F² using SHELXS-86⁸ and SHELXL-93.⁹ All non-hydrogen atoms except disordered atoms [O(15) and O(15'), O(16) and O(16'), 3 Cp rings] which were refined isotropically with site occupancies of 0.6 and 0.4, were refined by using anisotropic thermal factors, and all hydrogen atoms were positioned geometrically and refined using riding model. The

Table 2. Bond lengths [\AA] and angles [$^\circ$] for $[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2\text{Y}]$

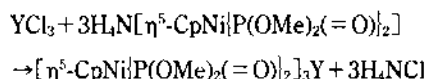
Y-O(1)	2.216(4)	Y-O(2)	2.238(4)
Y-O(3)	2.221(4)	Y-O(4)	2.223(4)
Y-O(5)	2.233(5)	Y-O(6)	2.205(4)
O(1)-P(1)	1.504(5)	O(2)-P(2)	1.508(5)
O(3)-P(3)	1.498(4)	O(4)-P(4)	1.511(5)
O(5)-P(5)	1.503(5)	O(6)-P(6)	1.502(5)
Ni(1)-P(1)	2.112(2)	Ni(1)-P(2)	2.126(2)
Ni(2)-P(4)	2.131(2)	Ni(2)-P(3)	2.131(2)
Ni(3)-P(5)	2.113(2)	Ni(3)-P(6)	2.127(2)
P(1)-O(7)	1.537(7)	P(1)-O(8)	1.656(7)
P(2)-O(10)	1.580(6)	P(2)-O(9)	1.624(6)
P(3)-O(12)	1.594(6)	P(3)-O(11)	1.596(6)
P(4)-O(14)	1.579(6)	P(4)-O(13)	1.620(6)
P(5)-O(15)	1.61(1)*	P(5)-O(16)	1.68(1)*
P(6)-O(17)	1.59(2)	P(6)-O(18)	1.610(6)
O(6)-Y-O(1)	96.9(2)	O(6)-Y-O(3)	172.2(2)
O(1)-Y-O(3)	89.9(2)	O(6)-Y-O(4)	92.8(2)
O(1)-Y-O(4)	170.0(2)	O(3)-Y-O(4)	80.6(2)
O(6)-Y-O(5)	81.2(2)	O(1)-Y-O(5)	91.3(2)
O(3)-Y-O(5)	94.9(2)	O(4)-Y-O(5)	92.6(2)
O(6)-Y-O(2)	86.8(2)	O(1)-Y-O(2)	82.0(2)
O(3)-Y-O(2)	97.9(2)	O(4)-Y-O(2)	96.1(2)
O(5)-Y-O(2)	165.5(2)	P(1)-Ni(1)-P(2)	96.32(8)
P(4)-Ni(2)-P(3)	97.36(8)	P(5)-Ni(3)-P(6)	95.48(8)
O(1)-P(1)-O(7)	106.7(3)	O(1)-P(1)-O(8)	110.3(4)
O(7)-P(1)-O(8)	96.5(5)	O(2)-P(2)-O(10)	107.0(3)
O(2)-P(2)-O(9)	108.3(3)	O(10)-P(2)-O(9)	97.1(4)
O(3)-P(3)-O(12)	107.2(3)	O(3)-P(3)-O(11)	108.9(3)
O(12)-P(3)-O(11)	93.4(4)	O(4)-P(4)-O(14)	106.6(3)
O(4)-P(4)-O(13)	108.6(3)	O(14)-P(4)-O(13)	97.3(4)
O(5)-P(5)-O(15)	107.8(6)*	O(5)-P(5)-O(16)	106.0(7)*
O(16)-P(5)-O(15)	92.4(5)*	O(6)-P(6)-O(17)	107.9(2)
O(6)-P(6)-O(18)	102.5(3)	O(17)-P(6)-O(18)	103.3(2)

Bond distances and angles with an asterisk are mean values calculated from disordered atoms, pair of O(15) and O(15') or pair of O(16) and O(16')

final cycle of the refinement converged with $R_1=0.054$ and $wR_2=0.121$. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Relative bond distances and angles are presented in Table 2.

Results and Discussion

Reaction of YCl_3 with 3 equivalent $\text{H}_4\text{N}[\eta^5\text{-CpNi}\{\text{P}(\text{OMe})_2(=\text{O})\}_2]$ in THF leads to the title compound.



The ^1H NMR spectrum of the compound shows that all Cp ring and methoxy groups are chemically equivalent. These data are not enough to explore the coordination environment around yttrium. Therefore X-ray crystal structure determination has been carried out. Figure 1 exhibits ORTEP drawing

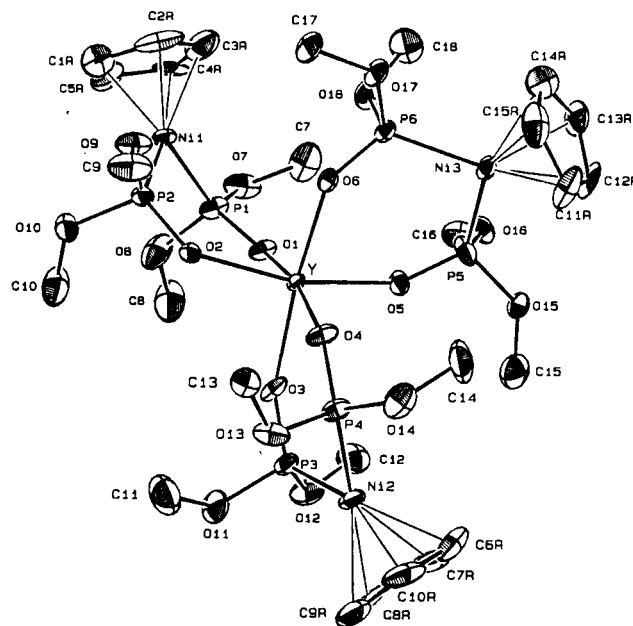


Figure 1. ORTEP drawing of 40% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity. And parameters for disordered atoms are the mean values.

and atomic labeling scheme of the compound. The coordination geometry around yttrium is pseudo-octahedral *via* three bidentate ligands [O(1), O(2), O(3), O(4), O(5), O(6)] because of small bite angles of 82.0(2), 80.6(2), 81.2(2) $^\circ$. Bond angles of O(6)-Y-O(3), O(4)-Y-O(1), and O(5)-Y-O(2) are 172.2(2), 170.0(2), and 165.5(2), which are nearly linear. Distances of Y-O(1), Y-O(2), Y-O(3), Y-O(4), Y-O(5), and Y-O(6) are 2.216(4), 2.238(4), 2.221(4), 2.223(4), 2.233(5), 2.205(4) \AA , respectively. The mean distance¹⁰ of Y-O is 2.22(1) \AA which are somewhat shorter than 2.38(6) \AA of average distance Y-O in nine-coordinate complex of (acac)₃Y(OH)₂¹¹ and are similar to 2.264(3) \AA of Y-O=P in Y[OP(n-Bu)₃][OSiPh₃]₃.⁷ Distances of P-O(1), P-O(2), P-O(3), P-O(4), P-O(5), and P-O(6) are 1.504(5), 1.508(5), 1.498(4), 1.511(5), 1.503(5), and 1.502(5) \AA . These mean separation¹⁰ between P and O attached yttrium atom is 1.504(5) \AA , which is slightly longer than P=O distance, 1.46(5) \AA .¹² These comparison reveals that Y-O bonds are somewhat partial double bonds. To our best knowledge, the title compound is a homoleptic six-coordinate complex of yttrium which is the first structurally characterized.

Acknowledgment. This research has been supported financially by the Korea Science and Engineering Foundation.

Supplementary Material Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms (2 pages), bond distances and angles (2 pages), anisotropic displacement parameters, hydrogen coordinate and isotropic displacement parameters (2 pages), and observed and calculated structure factors (20 pages) are available from J. H. J.

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