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Synthesis and X-Ray Crystal Structure of Bis[$(\eta^5\text{-Cp})\text{tris}(\text{-dimethylphosphito-P)cobalt-O,O',O''}]$ Yttrium(III)acetate

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Our recent investigation into the formation of early transition metal complexes containing O-donor tripodal ligands ($\text{L} = \text{CpCo}[\text{P}(\text{O})(\text{OMe})_2]_3$) have resulted in preparation of $\text{L}_2\text{MX}_{1-2}$,^{1,2} which are candidates as the starting compounds, to compare the chemical behavior of L to those of cyclopentadienyl or hydrotris(pyrazol-1-yl)borate ligands. Binding of carboxylate ligands to transition metals is a subject of considerable interest due to the various bonding modes such as unidentate, symmetrical or asymmetrical chelate, symmetrical *syn-syn* bridging, *anti-anti* single bridging, or *anti-syn* single bridging.³ Templeton and coworkers⁴ have reported preparation of $\text{Mo}(\text{CO})_2(\text{PEt})_3(\text{O}_2\text{CH})_2$, in which formate ligands are bonded to the metal as unidentate and bidentate. Carboxylate complexes of yttrium containing two hydrotris(pyrazol-1-yl)borate ligands have been synthesized and then characterized by spectroscopic methods but their exact bonding modes to yttrium are not determined clearly.⁵ Recently, syntheses of titanium complexes, that contained acetate ligands in bridging or chelating fashion, have been reported.⁶ So we are interested in the bonding patterns of the carboxylate ligands to YL_2 moiety. Here we wish to report the synthesis of an acetate complex of YL_2 and its bonding mode by X-ray diffraction study.

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 and NaO_2CCH_3 were purchased from Aldrich Co. and used as received. NaL was prepared by the literature method.⁷

^1H NMR spectrum was obtained in CDCl_3 and referenced to internal deuterated solvent and recalculated relative to TMS on a Bruker AM-300 spectrometer. IR spectrum was obtained on a Bomem Michelson 100 spectrometer as KBr pellet. Chemical analyses were carried out by the Chemical Analysis Laboratory at Korea Basic Science Institute.

Preparation of $[\eta^5\text{-CpCo}[\text{P}(\text{O})(\text{OMe})_2]_3]_2\text{Y}(\text{O}_2\text{CCH}_3)$.

20 mL of dry THF was introduced to a mixture of 0.49 g (1.0 mmol) of NaL and 0.1 g (0.5 mmol) of YCl_3 . The mixture was stirred at room temperature for 24 h resulting yellow solution and precipitate. The solution was transferred to 0.042 g (0.5 mmol) of NaO_2CCH_3 . The resulting suspension was stirred at room temperature for 2 days and then the precipitate was filtered off. The filtrate was evaporated *in vacuo* to afford yellow solid. Recrystallization of the crude product from a solvent pair of THF-hexane gives yellow crystals in 80% (0.8 g) yield.

Analysis: Calcd.(%) C; 27.43, H; 4.66 Found(%) C; 27.91, H; 4.61.

^1H NMR (CDCl_3): δ 5.02 (s, $2\text{C}_5\text{H}_5$, 10H), 83.60 (m, 12 $\text{H}_3\text{C-O-P}$, 36H), δ 1.18 (s, $\text{H}_3\text{C-C}$, 3H)

IR (cm^{-1}): 2942 (m), 2842 (w), 1570 (m), 1446 (m), 1180 (sh), 1136 (vs), 1108 (sh), 1016 (vs)

X-ray crystallographic analysis. An X-ray quality single crystal, $0.35 \times 0.35 \times 0.40$ mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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 $1.88\text{-}24.97^\circ$ 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 F using SHELXS-86⁸ and SHELX-76.⁹ All non-hydrogen atoms were refined by using anisotropic thermal factors, and all hydrogen atoms were positioned geometrically using riding model with fixed isotropic thermal factors ($U = 0.08 \text{ \AA}^2$). The final cycle of the refinement converged with $R = 0.066$ and $wR = 0.069$. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles are presented in Table 2.

Results and Discussion

$[\text{L}_2\text{YCl}]$, which is formed from the reaction of YCl_3 with 2 equivalent NaL in THF, reacts with NaO_2CCH_3 to afford the title compound.

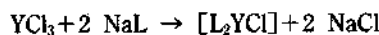


Table 1. Crystal data and structure refinement for $L_2Y(O_2CCH_3)$

Empirical formula	$C_{24}H_{48}Co_2O_{20}P_6Y$
Formula weight	1050.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a=11.569(2)$ Å $b=12.381(2)$ Å $c=16.601(2)$ Å $\alpha=94.95(3)$ Å $\beta=97.42(3)$ Å $\gamma=117.35(3)$ Å
Volume	$2065.5(5)$ Å ³
Z	2
Density (calculated)	1.689 Mg/m ³
Absorption coefficient	2.492 mm ⁻¹
F(000)	1072
Crystal size	0.35×0.35×0.40 mm
Theta range for data collection	1.88 to 24.97°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, 0 ≤ l ≤ 19
Reflections collected	5208
Refinement method	Full-matrix least-squares on F
Data/restraints/parameters	4100/0/478
Goodness-of-fit on F	0.900
Final R indices	R=0.0658, wR=0.0689
[I > 4σ(I)]	
Largest diff. peak and hole	1.458 and -2.055 e.Å ⁻³

$$w = 1.0000/(\sigma^2(F) + 0.00876 F^2)$$

The ¹H NMR spectrum of the compound shows a singlet at 5.02 ppm for 2 Cp rings(10H), a multiplet at 3.60 ppm for H₃C-O-P(36H), and a singlet at 1.18 ppm for H₃C-C(3H). Two stretching frequencies for the carbonyl group appear at 1570 and 1446 cm⁻¹ on the IR spectrum. However, in order to explore the coordination environment around yttrium, X-ray crystal structure determination has been carried out. Fig. 1 exhibits an ORTEP¹⁰ drawing and atomic labeling scheme of the compound. The coordination polyhedron around the yttrium is a distorted square antiprism, consisting of O(1), O(2), O(3), O(4), O(5), O(6) via two tripodal groups and O(19) and O(20) from chelating acetate ligand, because four atoms of O(1), O(2), O(20), and O(5) are not in the plane also four atoms of O(3), O(4), O(6), and O(19) are not coplanar due to stereo-rigidities of chelating tripodal and acetate groups. However, the lengths of O(1)-O(2), O(2)-O(20), O(20)-O(5), and O(5)-O(1) are in the range of 2.797(9) to 3.00(1) Å and four angles of these atoms are 82.1(3) through 90.0(3)° and the lengths of O(3)-O(4), O(4)-O(6), O(6)-O(19), and O(19)-O(3) are within 2.71(1) to 3.00(1) Å and four angles of these atoms are 82.7(3) through 90.0(3)°. Distances of Y-O(1), Y-O(2), Y-O(3), Y-O(4), Y-O(5), Y-O(6), Y-O(19), and Y-O(20) are 2.358(7), 2.350(5), 2.293(6), 2.287(6), 2.334(7), 2.414(8), and 2.423(8) Å, respectively. The mean distance of Y-O is 2.22(1) Å which are somewhat shorter than 2.38(6)

Table 2. Selected bond distances (Å) and angles (°) for $L_2Y(O_2CCH_3)$

Y -O1	2.358(7)	P3 -O3	1.497(5)
Y -O2	2.350(5)	P4 -O4	1.514(5)
Y -O3	2.293(6)	P5 -O5	1.509(5)
Y -O4	2.287(6)	P6 -O6	1.496(5)
Y -O5	2.334(7)	P1 -O7	1.600(11)
Y -O6	2.366(6)	P1 -O8	1.610(8)
Y -O19	2.414(8)	P2 -O9	1.604(8)
Y -O20	2.423(8)	P2 -O10	1.601(10)
CO1 -P1	2.168(3)	P3 -O11	1.611(12)
CO1 -P2	2.168(3)	P3 -O12	1.593(9)
CO1 -P3	2.186(3)	P4 -O13	1.601(9)
CO2 -P4	2.191(3)	P4 -O14	1.602(10)
CO2 -P5	2.167(3)	P5 -O15	1.606(9)
CO2 -P6	2.163(3)	P5 -O16	1.606(7)
P1 -O1	1.495(6)	P6 -O17	1.607(7)
P2 -O2	1.494(5)	P6 -O18	1.609(9)
O2 -Y -O1	73.6(2)	O8 -P1 -O1	110.7(4)
O3 -Y -O1	78.5(2)	O8 -P1 -O7	98.1(5)
O3 -Y -O2	79.0(2)	O9 -P2 -O2	108.7(4)
O4 -Y -O1	78.0(2)	O10 -P2 -O2	108.6(4)
O4 -Y -O2	110.4(2)	O10 -P2 -O9	100.3(4)
O4 -Y -O3	150.7(3)	O11 -P3 -O3	107.7(4)
O5 -Y -O1	75.5(2)	O12 -P3 -O3	109.1(4)
O5 -Y -O2	144.6(2)	O12 -P3 -O11	103.5(5)
O5 -Y -O3	78.3(2)	O13 -P4 -O4	108.2(4)
O5 -Y -O4	79.2(2)	O14 -P4 -O4	108.4(4)
O6 -Y -O1	143.5(2)	O14 -P4 -O13	103.3(4)
O6 -Y -O2	141.8(3)	O15 -P5 -O5	108.5(4)
O6 -Y -O3	110.7(2)	O16 -P5 -O5	110.9(4)
O6 -Y -O4	79.5(2)	O16 -P5 -O15	97.8(4)
O6 -Y -O5	72.3(2)	O17 -P6 -O6	110.1(4)
O19 -Y -O1	144.0(2)	O18 -P6 -O6	108.2(4)
O19 -Y -O2	74.6(2)	O18 -P6 -O17	100.5(4)
O19 -Y -O3	79.4(2)	P1 -O1 -Y	138.7(4)
O19 -Y -O4	129.5(2)	P2 -O2 -Y	138.5(5)
O19 -Y -O5	126.6(2)	P3 -O3 -Y	137.4(4)
O19 -Y -O6	71.5(2)	P4 -O4 -Y	135.5(4)
O20 -Y -O1	127.8(2)	P5 -O5 -Y	139.0(4)
O20 -Y -O2	71.7(2)	P6 -O6 -Y	139.3(5)
O20 -Y -O3	129.7(2)	C7 -O7 -P1	123.2(<1)
O20 -Y -O4	79.0(2)	C19 -O19 -Y	93.5(6)
O20 -Y -O5	142.9(2)	C19 -O20 -Y	93.4(6)
O20 -Y -O6	74.5(2)	O20 -C19 -O19	119.0(<1)
O20 -Y -O19	54.1(2)	C20 -C19 -O19	121.6(<1)
O7 -P1 -O1	107.4(4)	C20 -C19 -O20	119.4(<1)

Å of the average distance Y-O in the nine-coordinate complex (acac)₃Y(OH₂)₃¹² and are similar to 2.264(3) Å for Y-O=P in Y[OP(n-Bu)₃][OSiPh₃]₃.¹³ Distances of P-O(1), P-O(2), P-O(3), P-O(4), P-O(5), and P-O(6) are 1.495(6), 1.494(5), 1.497(5), 1.514(5), 1.509(5), and 1.496(5) Å. The mean separation¹¹ between P and O attached yttrium atom is 1.501(8) Å, which is slightly longer than P=O distance, 1.46(5) Å.¹⁴ This comparison reveals that Y-O bonds have partial double bond cha-

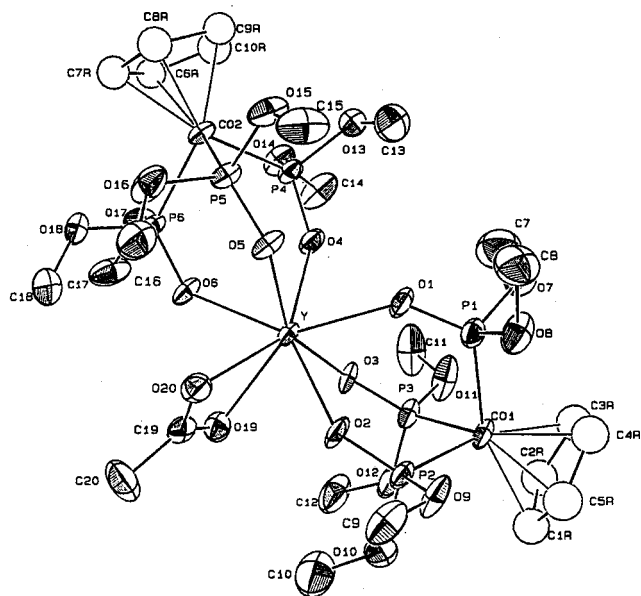


Figure 1. ORTEP drawing of 40% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity. And parameters for disordered atoms are the mean values.

acter. Clearly the acetate ligand is bonded to Y in an isobidentate type from the same distances of Y-O(19) and Y-O(20) within experimental error.

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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 (2 pages), hydrogen coordinate and isotropic displacement parameters (1 page), and observed and calculated structure factors (17 pages) are available from J. H. J.

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Thermal Rearrangement of 3-Trimethylsilyl-1-Pyrazoline

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Several examples of 1,3- and 1,5-rearrangement of a silyl group to a heteroatom have been reported. These comprise 1,3-migrations from carbon to oxygen,¹ nitrogen to oxygen,² nitrogen to nitrogen,^{2b,3} nitrogen to sulfur,^{2b} and 1,5-migrations from oxygen to oxygen⁴ and nitrogen to nitrogen.⁵ The unimolecular reaction kinetics of a suprafacial 1,3-sigmatropic rearrangement involving an antisymmetric 3p silicon orbital of silyl group in allylsilanes has been reported.⁶ There is a precedent for 1,3-trimethylsilyl shift from carbon to nitrogen over a pyrazoline ring.⁷⁻¹⁰ Cycloaddition of diazomethane to vinyltrimethylsilane would provide the desired starting material, 3-trimethylsilyl-1-pyrazoline, **1**.¹⁰ During the course of purification of **1** on a preparative GC with an OV-17 (20% on Chromosorb W 80/100, 1/4 in×22 ft) the complete isomerization to 1-trimethylsilyl-2-pyrazoline, **2** was discovered. To our knowledge, the kinetics of 1,3-silyl group migration from carbon to nitrogen over a pyrazoline ring has not reported yet.

We wish to report the kinetics of thermally induced 1,3-rearrangement of a trimethylsilyl group from carbon to nitrogen over a pyrazoline ring. The isomerization of **1** to **2** has been examined kinetically by means of ¹H NMR spectroscopy. The effect of solvent on the rate of rearrangement from **1** to **2** has been briefly considered. Thermal elimination of dinitrogen from 3-trimethylsilyl-1-pyrazoline leads to cyclopropyltrimethylsilane, allyltrimethylsilane, and *E*- and *Z*-propenyltrimethylsilane at higher temperatures (417-478 °C).¹¹ However, thermolysis of **1** in a sealed capillary tube at lower temperatures (70-100 °C) leads to **2** without decomposition of the starting material, **1**.