or slightly cross-linked polymer. Thus, it is apparently essential to the production of a high-molecular-weight polysilane that a disilane should have at least one SiH_3 moiety. The sterically less bulky silane **2** produced the higher-molecular-weight dehydrocoupling product when compared to **1**. The allyl group on **1** could not accelerate the reaction rate unlike the titanocene-catalyzed dehydropolymerization of phenylsilane in the presence of cyclohexene.[5b] The dehydrocoupling study of other types of alkylene disilanes using various transition metal catalysts is in progress and will be reported in the near future.

In conclusion, this work describes the preparation and dehydrocoupling of ethylene disilanes, 2,5-disila-7-octene **1** and 2,5-disilahexane **2**, catalyzed by titanocene complex generated *in situ* from Cp_2TiCl_2/Red-Al. The silanes **1** hydrogenated and/or dehydrocoupled to produce cooligomer (M_n=410) of **1** and 2,5-disilaoctane with a silm chance of hydrosilation. The silanes **2** dehydrocoupled to produce a non-cross-linked or slightly cross-linked polysilane with an average molecular weight M_w of 2030 and a polydispersity of 2.6.

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Synthesis and Characterization of (L)Zr(L)$_2$Zr(L). (L=CpCo{P(=O)(OMe)$_2$}$_2${P(=O)(OMe)(O)})

Iee Yeung Cho, Hwan Jin Yeo*, and Jong Hwa Jeong*

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

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The anionic Cobalt(III)-based oxygen tripod L_{OEt} (L_{OEt}=[CpCo{P(=O)(OEt)$_2$}$_3$]$^-$), delveloped by Klaui and coworkers, can form stable complexes with various transition metals.[1] The synthesis and X-ray structures of $Zr(L_{OEt})Cl_3$ and $U(L_{OEt})_2Cl_2$ have been reported,[2] which are expected as the starting compounds to examine the property of the oxygen tripod ligand compared to Cp or Cp derivaties. So we have attempted to obtain $Zr(L_{OMe})_2Cl_2$ (L_{OMe}=[CpCo{P(=O)(OMe)$_2$}$_3$]$^-$) from the feasible reaction of $ZrCl_4$ with 2 epuivalent NaL_{OMe}. However, (L)Zr(L)$_2$Zr(L) has been isolated surprisingly at room temperature, which is the second example of the unusual dimer in an unusual bridging fashion of tripod ligand shown in (L_{OEt})Y[CpCo{P(=O)(OEt)$_2$}$_2${P(=O)(OEt)(O)}]$_2$Y(L_{OEt}) formed at high temperature.[3] Herein we report the preparation and X-ray structure of the title compound.

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. $ZrCl_4$ was purchased from Aldrich Co. and used as received. L_{OMe} was prepared by the literature method.[4]

^1H and ^{31}P NMR spectra were obtained in $CDCl_3$ and referenced to internal deuterated solvent and recalculated relative to TMS and to external 85% H_3PO_4 on a Bruker AM-300 spectrometor. Chemical analyses were carried out by

Table 1. Crystal data and structure refinement for (L)Zr(L)$_2$Zr (L)·$2CH_2Cl_2$

Empirical formula	$C_{40}H_{80}Co_4O_{36}P_{12}Zr_2 \cdot 2CH_2Cl_2$
Formula weight	2096.7
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 15.031(3) Å
	b = 16.202(3) Å β = 91.742(8) Å
	c = 16.130(3) Å
Volume	3926(1) Å^3
Z	2
Density (calculated)	1.773 Mg/m^3
Absorption coefficient	1.544 mm^{-1}
F(000)	2120
Crystal size	0.40×0.45×0.50 mm
Theta range for data collection	2.71 to 24.64°
Index ranges	$0 <= h <= 17$, $-18 <= k <= 0$,
	$-18 <= l <= 18$
Reflections collected	5865
Independent reflections	5728 [R(int) = 0.0543]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5728/1/451
Goodness-of-fit on F^2	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.0980$
R indices (all data)	$R_1 = 0.0369$, $wR_2 = 0.0983$
Largest diff. peak and hole	0.634 and −0.748 eÅ^{-3}

Table 2. Relevant Bond lengths [Å] and angles [°] for (L)Zr(L)$_2$ Zr(L)·$2CH_{2Cl2}$

Zr-O(3)	2.027(3)	Zr-O(7)	2.112(3)
Zr-O(5)′	2.121(3)	Zr-O(4)	2.134(3)
Zr-O(1)	2.186(3)	Zr-O(6)	2.190(3)
Zr-O(2)	2.224(3)	Co(1)-P(1)	2.1435(11)
Co(1)-P(2)	2.1477(12)	Co(1)-P(3)	2.2078(11)
P(1)-O(1)	1.510(3)	P(1)-O(9)	1.599(3)
P(1)-O(8)	1.600(3)	P(2)-O(2)	1.504(3)
P(2)-O(11)	1.585(4)	P(2)-O(10)	1.601(3)
P(3)-O(18)	1.481(3)	P(3)-O(3)	1.568(3)
P(3)-O(12)	1.622(3)	Co(2)-P(5)	2.1527(13)
Co(2)-P(6)	2.1536(13)	Co(2)-P(4)	2.1948(11)
P(4)-O(5)	1.513(3)	P(4)-O(4)	1.531(3)
P(4)-O(13)	1.604(3)	P(5)-O(6)	1.511(3)
P(5)-O(15)	1.584(4)	P(5)-O(14)	1.590(3)
P(6)-O(7)	1.529(3)	P(6)-O(16)	1.592(3)
P(6)-O(17)	1.596(3)		
O(3)-Zr-O(7)	175.06(10)	O(3)-Zr-O(5)′	89.92(11)
O(3)-Zr-O(1)	87.72(10)	O(3)-Zr-O(2)	81.84(10)
O(3)-Zr-O(4)	97.91(10)	O(3)-Zr-O(6)	97.48(11)
O(7)-Zr-O(5)′	91.74(11)	O(7)-Zr-O(1)	88.35(10)
O(7)-Zr-O(2)	94.15(11)	O(7)-Zr-O(4)	87.02(10)
O(7)-Zr-O(6)	83.63(11)	O(5)′-Zr-O(1)	72.42(10)
O(1)-Zr-O(2)	72.98(10)	O(6)-Zr-O(2)	68.42(10)
O(4)-Zr-O(6)	72.78(10)	O(5)′-Zr-O(4)	74.26(10)
P(1)-Co(1)-P(2)	87.73(5)	P(1)-Co(1)-P(3)	91.39(4)
P(2)-Co(1)-P(3)	93.98(4)	P(5)-Co(2)-P(6)	90.32(5)
P(5)-Co(2)-P(4)	88.74(5)	P(6)-Co(2)-P(4)	94.27(4)

the Chemical Analysis Laboratory at KBSC.

Preparation of (L)Zr(L)$_2$Zr(L). To a mixture of $ZrCl_4$ (0.93 g, 4.0 mmol) and NaL_{OMe} (3.79 g, 8.0 mmol) 50 mL of THF was introduced and then resulting suspension was stirred for 24 h at room temperature. Volatile merterials were removed under reduced pressure. Extraction of the solid with dichloromethane afforded yellow solution. The solution was concentrated and layered by hexane to yield yellow crystalline(3.06 g, 73%).

Anal. Calcd for $Zr_2Co_2P_{12}O_{36}C_{40}H_{80} \cdot 2CH_2Cl_2$: C, 24.05; H, 4.04. Found: C, 23.90; H, 4.13. ^{1}H NMR ($CDCl_3$): δ 5.19 (s, C_5H_5, 5H), δ 3.9 (m, $(H_3CO)P(O)_2$, 3H), δ 3.7 (m, $(H_3CO)_2P(O)$, 12H). ^{31}P NMR ($CDCl_3$): δ 138.3 (d, $^2J_{PP} = 138$ Hz), δ 82.3 (t, $^2J_{PP} = 136$ Hz).

X-ray crystallographic analysis. A X-ray quality single crystal, 0.40×0.45×0.50 mm, was mounted in a thin-walled glass capillary on an Enraf-Nonius CAD-4 diffractometer, unit cell parameters were determined by least-squares analysis of 25 reflections ($20° < 2\theta < 26°$) by using $\omega/2\theta$ scan mode. Intensity data were collected with MoKα radiation ($\lambda = 0.71073$ Å). Three standard reflections were monitored every 1 h 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^2 using SHELXS-86[5] and SHELXL-93.[6] All non-hydrogen atoms were refined by using anisotropic thermal factors, and all hydrogen atoms were positioned geometrically and refined using riding model. The final cycle of the refinement converged with $R_1 = 0.037$ and $wR_2 = 0.098$. 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 $ZrCl_4$ with 2 equivalent NaL_{OMe} in the THF at room temterature followed by extraction with dichloromethane leads to the isolation of a yellow crystalline. The ^{1}H NMR spectrum of the title compound exhibits two inequivalent phosphonate methyl groups and equivalent Cp rings. The ^{31}P NMR spectrum shows two inequivalent phosphorus resonances which show phosphorus-phosphorus coupling. These NMR spectral results were not expected in unsual Yttrium dimer containing L_{OEt} which was formed from the reaction of YCl_3 with 2 equivalent L_{OEt} at high temperature.[3] In order to determine the structure of the compound, an X-ray crystal structure determination was carried out. The crystal structure clearly shows the molecule to consist of a dimeric arrangement of seven-coordinate zirconium centers (pentagonal bipyramid structure) and the absence of Cl atoms and 4 phosphonate methyl groups (Figure 1). This sructure reveals the cleavage of a phosphonate methyl

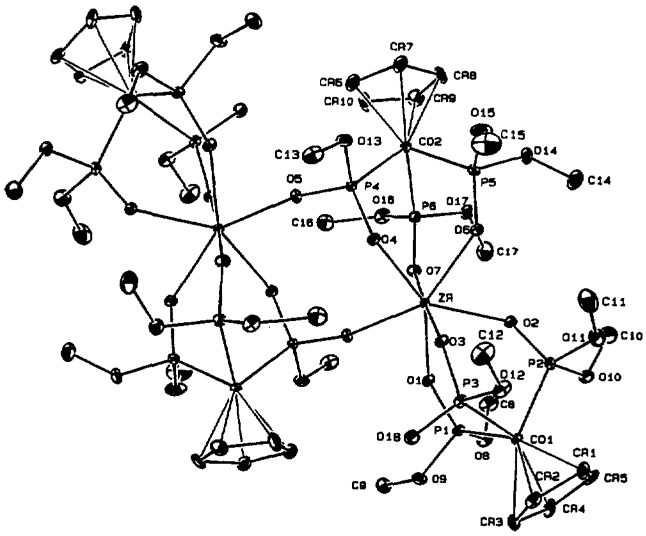

Figure 1. Molecular structure of 30% probability displacement elipsoide. Hydrogen atoms are ommitted for clarity.

groups by direct attack of Cl^-, making possible the dimeric linkage and the second cleavage of other phosphonate methyl group, forming a new P=O bond. Zr-O (2.112(3) to 2.224(3) Å) distances between zirconium and the bridging or nonbridging phosphonate oxygens are not distinguishable except Zr-O (3)(2.027(3) Å) wich is somewhat shorter than others, reflecting formation of a new terminal P=O bond. The P-O distances (1.511(3) to 1.529(3) Å) in the bridging Zr-O-P linkage are similar to those (1.504(3) to 1.510(3) in the nonbridging Zr-O-P linkage as well as P-O distances (1.500(7) and 1.527(7) Å) in the isostructural oxygen tripod complex $[L_{OEt}YCpCo(P(=O)(OEt)_2)_2(P(=O)(OEt)(O))_2YL_{OEt}]^3$ except P (3)-O(3)(1.568(3) Å) which is somewhat longer than others, also reflecting generation of the terminal P=O bond.

A possible reaction pathway followed in the present reaction can be postulated by examining results reported on the related $[L_{OEt}YCpCo(P(=O)(OEt)_2)_2(P(=O)(OEt)(O))_2YL_{OEt}]$ complex,[3] in which system direct attack on the phosphonate ethyl group by Cl^- *via* an Arbuzov-type dealkylation, leading to the formation of phosphonate-bridged dimer took place. Specially, interesting feature in this study is that the second Arbuzov-type demethylation takes place in zrconium(IV) system which has another Cl^- compared to yttrium(III) system to form a new terminal P=O bond from P-OMe, resulted in the demethylation processes on the bridged and nonbridged tripod ligands. On the basis of experimental spectroscopic and crystallographic results, the overall reaction stoichiometry is proposed as following equation:

$$2\ ZrCl_4 + 4\ NaL_{OMe} \rightarrow (L)Zr(L)_2Zr(L) + 4\ NaCl + 4\ MeCl$$

Generated MeCl during the reaction was idendified by GC-MS. To our knowledge, this is the frist example of double dealkylation reactions on two tripod ligands in a single compound and is the second example of the formation of the unusual dimerization through bridged tripod.

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Supplementary Material Available. Tables of atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinate and isotropic displacement parameters (5 pages); table of observed and calculated structure factors (19 pages) are available from J. H. J..

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