

ppm): 0.03 (s, 6H, Si(CH₃)₂), 0.83 (s, 9H, SiC(CH₃)₃), 1.18 (dd, *J*=7.32, 7.56 Hz, 6H, CH₃), 1.35 (d, *J*=11.47 Hz, 6H, C(CH₃)₂), 2.60-2.70 (m, 4H, SCH₂), 3.75 (dd, *J*=6.34, 4.88 Hz, 2H, H-4), 3.87 (d, *J*=4.64 Hz 1H, H-1), 4.04-4.10 (m, 1H, H-3), 4.18 (dd, *J*=4.64, 4.64 Hz, 1H, H-2).

4-O-tert-Butyldimethylsilyl-2,3-O-isopropylidene-L-threose (7). To the mixture of **6** (200 mg, 0.51 mmol) and 2,6-lutidine (0.35 mL, 3 mmol) in aqueous acetonitrile was added NBS (0.25 g, 1.4 mmol) until yellow color was remaining. The mixture was washed with 1 M Na₂SO₃ solution, and extracted with CH₂Cl₂/hexane (1:1) solution. The collected organic layer was dried, filtered, and evaporated to yield crude aldehyde **7** (0.13 g, 0.48 mmol) which can be usually used for the further reaction without purification. ¹H NMR (CDCl₃, ppm): 0.03 (s, 6H, Si(CH₃)₂), 0.83 (s, 9H, SiC(CH₃)₃), 1.35 (d, *J*=11.47 Hz, 6H, C(CH₃)₂), 3.75 (dd, *J*=6.34, 4.88 Hz, 2H, H-4), 4.04-4.10 (m, 1H, H-3), 4.18 (dd, *J*=1.8, 4.64 Hz, 1H, H-2), 9.72 (d, *J*=1.8 Hz, 1H, H-1). IR (cm⁻¹): 3464, 2935, 1710, 1464, 1377, 1259, 1182, 1091.

Acknowledgment. This research was supported by Korean Science and Engineering Foundation (951-0301-060-2).

References

- (a) Lichtenthaler, F. W. *Carbohydrates as Organic Raw Materials*, 1991, Weinheim, VCH, F. R. G. (b) Ogura, H.; Hasegawa, A.; Suami, T. *Carbohydrates* 1992, Weinheim, VCH, F. R. G.
- (a) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *J. Org. Chem.* 1989, 54, 693. (b) Marshall, J. A.; Selesky, B. M.; Luke, P. *J. Org. Chem.* 1994, 59, 3413. (c) Mukaiyama, T.; Suzuki, K.; Yamada, T.; Tabusa, F. *Tetrahedron* 1990, 46, 265. (d) Cohen, N.; Banner, B. L.; Lopresti, R. J.; Wong, F.; Rosenberger, M.; Liu, Y.; Thom, E.; Liebman, A. A. *J. Am. Chem. Soc.* 1983, 105, 3661. (e) Gypser, A.; Flasche, M.; Scharf, H. *Liebigs Ann. Chem.* 1994, 775.
- Isbell, H. S.; Frush, H. L. *Carbohydr. Res.* 1979, 72, 301.
- Perin, A. S. *Methods Carbohydr. Chem.* 1962, 1, 67.
- (a) Mukaiyama, T.; Suzuki, K.; Yamada, T. *Chem. Lett.* 1982, 929. (b) Mukaiyama, T.; Suzuki, K.; Yamada, T.; Tabusa, F. *Tetrahedron* 1990, 46, 265.
- Kusakabe, M.; Sato, F. *Chem. Lett.* 1986, 1473.
- Baxter, J. M.; Perkin, A. S. *Can. J. Chem.* 1960, 38, 2217.
- Lerner, L. M. *Carbohydr. Res.* 1969, 9, 1.
- Shah, R. H. *Carbohydr. Res.* 1986, 155, 212.
- Buchanan, J. G.; Edgar, A. R.; Hewitt, B. D. *J. Chem. Soc. Perkin Trans. 1*, 1987, 1, 2371.
- Collins, P. M. *Carbohydrates*; Chapman and Hall, 512.
- (a) van Es, T. *Carbohydr. Res.* 1974, 32, 370. (b) Dalley, O. T.; Mcilroy, R. J. *J. Chem. Soc.* 1949, 555.

Synthesis and Properties of Low Molecular Weight π -Conjugated Poly(2,5-diethynylthiophene)

Young Tae Park*, Il Kwon Seo, and Yong-Rok Kim[†]

Department of Chemistry, Keimyung University,
Taegu 704-701, S. Korea

[†]Department of Chemistry, Yonsei University,
Seoul 120-749, S. Korea

Received December 23, 1995

Conjugated polymers have received considerable attention as advanced materials in recent years.¹ These polymers could be widely used as electronic, photonic, and optical materials.² Conjugated polymeric materials such as polyacetylene, polypyrrole, polyaniline, and polythiophene, etc., have been intensively studied.³

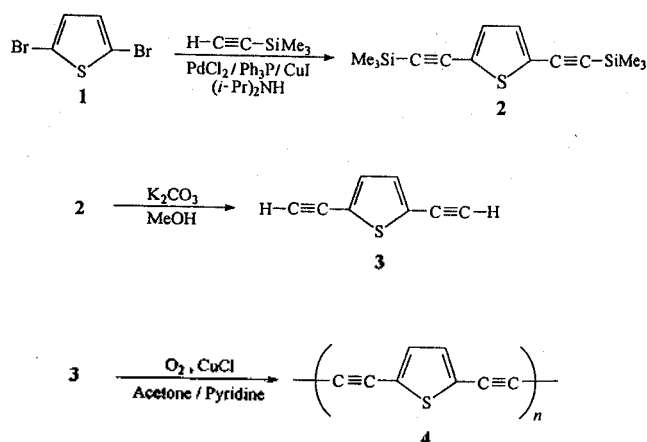
Recently, polymers conjugated with thiophene and diacetylene functionalities were reported.⁴ However, the unsubstituted diethynylthiophene polymer prepared by oxidative polymerization in pyridine with copper(I) chloride and oxygen^{5,6} turned out to be insoluble in usual organic solvent.⁷

Here we wish to describe the preparation and properties of low molecular weight poly(2,5-diethynylthiophene), which is soluble in organic solvents.

Results and Discussion

The synthetic route for the monomer of 2,5-diethynylthiophene (**3**) is outlined in Scheme 1.

The synthesis of **3** involves two steps: (a) the displacement of 2,5-dibromothiophene (**1**) with trimethylsilylacetylene, and (b) the subsequent cleavage of the trimethylsilyl protecting group to **3**.^{8,9} Trimethylsilylacetylene easily displaced the bromines of **1** in the presence of palladium(II) chloride, triphenylphosphine, copper(I) iodide in diisopropylamine to yield 2,5-bis[2'-(trimethylsilyl)ethynyl]thiophene (**2**). The desilylation reaction of **2** was accomplished with potassium carbonate in methanol at ambient temperature to obtain mono-



Scheme 1.

*To whom all correspondence should be addressed.

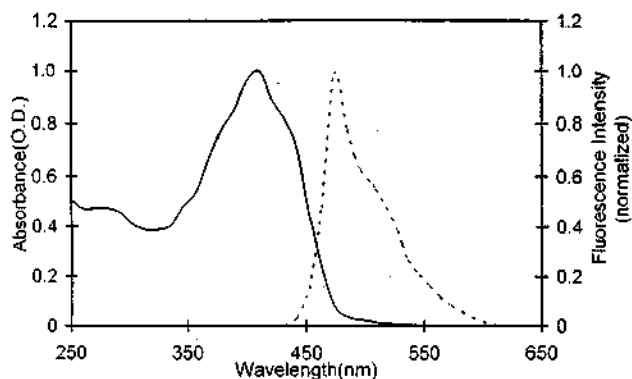


Figure 1. UV-visible absorption spectrum (—) and fluorescence emission spectrum (---) of 4 in THF.

mer 3.

It has been reported that oxidative polymerization of 2,5-diethynylthiophene in pyridine gave a polymer which was insoluble in usual organic solvents.^{4,10} The Glaser oxidative polymerization of 3 was carried out by using a cosolvent of acetone and pyridine (10:1 in v/v) in the presence of cuprous chloride with oxygen bubbling through the reaction mixture (Scheme 1). The dark brown polymer 4 was obtained in 26% yield with average molecular weights in the range of 1,500/670-2,300/1,880 (\bar{M}_w/\bar{M}_n). Polymer 4 had a solubility on the order of 10^{-4} M in organic solvents such as tetrahydrofuran and chloroform at room temperature. This solubility is probably due to the low molecular weights of 4. This permits us to perform studies of the polymer properties in solution phase. The UV-visible spectrum of 4 in THF was obtained as shown in Figure 1.

A strong absorbance maximum, centered λ_{max} of 410 nm, appears in the UV absorption band of 340-480 nm. The molar absorptivity at the 410 nm was 1.0×10^5 L/(mol·cm), which might be attributed to the π -conjugation of thiophene and diacetylene groups in polymer main chain. The fluorescence spectrum of 4 at the excitation wavelength of 450 nm in THF solvent is shown as the dotted line in Figure 1. The fluorescence spectrum shows a strong emission peak at λ_{max} of 475 nm with the emission band between 440 and 610 nm. This emission peak might be also due to the $\pi \rightarrow \pi^*$ transition of π -conjugation system in 4 through polymer main chain. In the IR spectrum of 4, the characteristic C \equiv C stretching frequency appears at 2100-2200 cm^{-1} .¹¹

A broad large exothermic peak (108 cal/g) centered at 152 °C in the range of 96-235 °C was observed from DSC as shown in Figure 2.

The exotherm is probably associated with the cross-linking reaction of the diacetylene group to form fused polycyclic aromatic materials.¹² The thermal stability of polymer 4 in nitrogen atmosphere was determined by TGA. The TGA thermogram of 4 is shown in Figure 3.

Polymer 4 was stable up to 410 °C without any weight loss. Despite its low molecular weight, this high thermal stability is also probably attributed to the cross-linking reaction of the diacetylene group to form fused polycyclic aromatic materials,¹² which is consistent with the result of DSC thermogram. Rapid weight loss of 45% of the initial sample weight occurs between 420 and 660 °C. Between 660 and 900

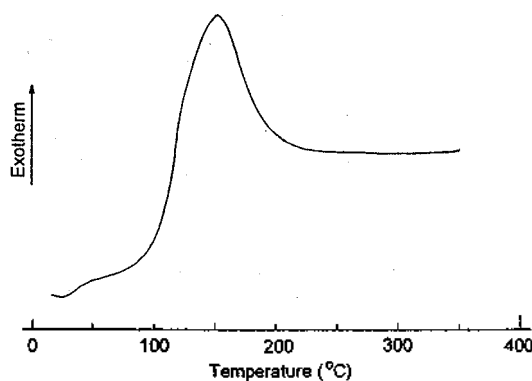


Figure 2. DSC thermogram of 4 in nitrogen.

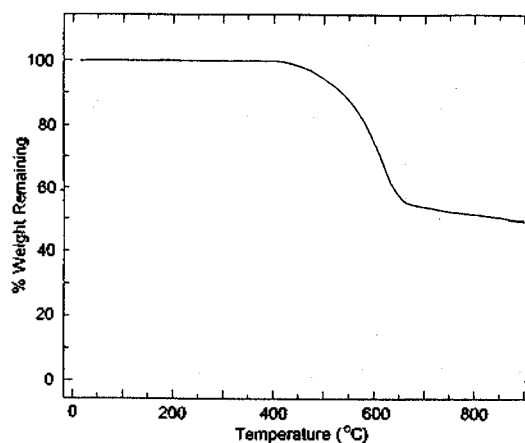


Figure 3. TGA thermogram of 4 in nitrogen.

°C an additional 5% weight loss occurs. A residue amounting to 50% of the initial weight remains when the sample is heated up to 900 °C.

In conclusion, low molecular weight 1,500/670-2,300/1,880 (\bar{M}_w/\bar{M}_n) poly(2,5-diethynylthiophene) has been prepared and is thermally stable up to 410 °C in nitrogen. The polymer 4 in THF solvent was found to have a strong absorbance at λ_{max} of 410 nm with a molar absorptivity of 1.0×10^5 L/(mol·cm) in UV-visible spectrum. A strong emission peak at the wavelength of 475 nm was detected in the fluorescence spectrum. Both absorption and emission spectra indicate strongly that the polymer 4 is π -conjugated through the polymer main chain. By using an ultrafast fluorescence spectroscopy, the molecular energy dynamics of the polymer is under investigation.

Experimental Section

All chemicals were purchased from Aldrich Chemicals Inc. Tetrahydrofuran (THF), *n*-pentane, *n*-hexane, and diethyl ether were distilled from sodium/benzophenone ketyl prior to use. Diisopropylamine was distilled from KOH before use. All glassware was dried overnight in an oven at 120 °C. The apparatus was assembled and then flamed-dried under argon.

Reactions were monitored by analytical gas liquid chromatography (GLC) on a Hewlett Packard 5890 II equipped with

HP-1 capillary column (0.53 mm×30 m) coated with cross-linked methyl siloxane gum and an FID detector. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shifts were measured using tetramethylsilane as an internal standard. IR spectra were recorded by a Shimadzu IR 430 or a Bruker IFS-48 FTIR spectrophotometers. UV-visible spectra were obtained on a Hewlett Packard 8452A or a Shimadzu UV-106A spectrophotometers. Fluorescence emission spectra were measured by a Hitachi F-2000 spectrofluorometer. Low resolution mass spectra were measured on a Mass Hewlett Packard 5971A instrument by EI ionization at 70 eV. GPC analyses were performed on a Waters Model 510 gel permeation chromatography with a Waters Styragel HR 3 column and a refractive index detector. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_n 580, 3250, 10100, and 28500 whose \bar{M}_w/\bar{M}_n are less than 1.2. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of polymer samples were performed on DSC-50 and TGA-50 Shimadzu thermal analysis systems, respectively. The temperature program for the analysis was from room temperature with a heating rate of 10 °C/min to 400 °C for DSC or to 900 °C for TGA with nitrogen flow rate of 20 mL/min. Elemental analyses were performed by a Fisons EA 1108 elemental analyzer.

2,5-Bis[2'-(trimethylsilyl)ethynyl]thiophene (2).^{7,8}

To a solution of 2,5-dibromothiophene (1) (25.2 g, 0.10 mol), triphenylphosphine (1.75 g, 6.7 mmol) and diisopropylamine (200 mL) in a flame-dried three-neck round bottom 1-L flask equipped with a mechanical stirrer, a reflux condenser, and a heating mantle were added copper(I) iodide (0.075 g, 0.39 mmol), palladium(II) chloride (0.15 g, 0.84 mmol), trimethylsilylacetylene (25 g, 0.26 mmol), and diisopropylamine (200 mL) under an argon atmosphere. The reaction mixture was allowed to warm to 40 °C for 2 h and then heated to reflux for 12 h until GC analysis indicated that all starting material had disappeared. The solution was allowed to cool to room temperature and filtered to remove the precipitated diisopropylammoniumbromide salt. The solvent was removed by evaporation under reduced pressure and the residue was taken up in methylene chloride. The organic layer was washed with 5% HCl solution, followed by water twice, dried over anhydrous MgSO_4 , filtered, and concentrated at reduced pressure. The crude product was dissolved in *n*-hexane and was purified by chromatography on a silica gel column. *n*-Hexane was used as the eluent. The product 2 of 19.1 g, 70% yield, was obtained. ^1H NMR (300 MHz, CDCl_3) δ 7.04 (s, 2H), 0.23 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3) δ 132.2, 124.4, 99.9, 96.8, 0.10; IR (KBr) ν 2961, 2146, 1558, 1421, 1264, 1171, 1006, 800 cm^{-1} ; MS *m/e* (relative intensity) 276 [M^+ , 48], 261 [($\text{M}-\text{CH}_3$) $^+$, 100], 123 (22), 73(18).

2,5-Diethynylthiophene (3).^{7,8} To a stirred solution of 3 (10.0 g, 36 mmol) in methanol (200 mL) in a flame-dried three-neck 250-mL round bottom flask equipped with a reflux condenser, a gas inlet, and Teflon covered magnetic stirring bar was added K_2CO_3 (0.27 g, 2.0 mmol). The solution was stirred at room temperature for 3 h until GC analysis indicated that the reaction was complete. The reaction mix-

ture was concentrated and extracted into *n*-pentane (40 mL). The *n*-pentane extract was washed with water (100 mL), dried over anhydrous MgSO_4 , and filtered. The volatile solvent was removed by evaporation under reduced pressure and the residue was carefully distilled at reduced pressure. A fraction, bp 32-34 °C/0.6 mmHg, 2.4 g, 52% yield, was obtained. ^1H NMR (300 MHz, CDCl_3) δ 7.11 (s, 2H), 3.35 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 132.6, 123.5, 82.1, 76.1; IR (KBr) ν 2959, 2928, 2109, 1554, 1438, 1215, 1005, 761 cm^{-1} ; MS *m/e* (relative intensity) 132 (M^+ , 100), 82 (15), 69 (27).

Poly(2,5-diethynylthiophene) (4). A flame-dried three-neck 500-mL round bottom flask equipped with a reflux condenser, a heating mantle, and Teflon covered magnetic stirring bar was charged with CuCl (0.75 g, 7.6 mmol) and acetone (180 mL). The well stirred suspension was slowly heated to 30 °C while the addition funnel was charged with a solution of acetone (20 mL) and pyridine (20 mL); 20 mL of this solution was added to the flask. The dark green mixture was stirred for 10 min before the compound 3 (0.99 g, 7.5 mmol) and 10 mL of the acetone/pyridine mixture was added. The mantle was removed when a small exotherm was observed. After a further stirring for 10 min, oxygen bubbling through the reaction mixture was begun. The oxygen flow was continued throughout the rest of the reaction. After the acetone/pyridine was added completely, a heating mantle was used to maintain temperature at 30-40 °C for an additional 6 h. The work-up was conducted under yellow light to prevent UV-induced cross-linking. The product was precipitated by the addition of methanol (20 mL) and 20% aqueous HCl (20 mL), and isolated by decantation. The crude polymer was redissolved in chloroform (100 mL), washed with 10% aqueous HCl and deionized water, dried over anhydrous MgSO_4 , and filtered. The chloroform solution was concentrated and the polymer was reprecipitated by addition of methanol (100 mL) and dried under reduced pressure. Polymer 4, a brown powder, 0.26 g, 26% yield, was obtained. This process was repeated. In this way, polymer 4 was obtained with molecular weights of 1500/670, 2090/1710, and 2300/1880 (\bar{M}_w/\bar{M}_n). ^1H NMR (300 MHz, CDCl_3) δ 7.26 (s); IR (KBr, pellet) ν 2960, 2175, 2139, 1425, 1264, 1092, 1027, 800 cm^{-1} . Elemental Anal. Calcd for $(\text{C}_8\text{H}_2\text{S})_n$: C, 73.8; H, 1.6; S, 24.6; Found: C, 72.9; H, 1.9; S, 26.3. Thermal analyses data were described in the Results and Discussion.

Acknowledgment. The present study was supported by a grant (Project No. BSRI-94-3424) from the Basic Science Research Institute Program, Ministry of Education. Y.R.K. thanks the Korea Science and Engineering Foundation (KOSEF 941-0300-007-2) for the partly financial support.

References

- Salaneck, W. R.; Lundström, I.; Rånby, B. Eds. *Conjugated Polymers and Related Materials-The interconnection of Chemical and Electronic Structure*; Oxford University Press: Oxford, 1993.
- Clery, D. *Science* 1994, 263, 1700.
- Saunders, B. R.; Fleming, R. J.; Murray, K. S. *Chem. Mater.* 1995, 7, 1082.
- Rutherford, D. R.; Stille, J. K.; Elliott, C. M. *Polym. Prepr.*

- (Am. Chem. Soc., Div. Polym. Chem.) 1990, 31, 643.
- Hay, A. S. *J. Polym. Sci., Polym. Chem. Ed.* 1969, 7, 1625.
 - Hay, A. S.; Bolon, D. A.; Leimer, K. R.; Clark, R. F. *J. Polym. Sci., Part B* 1970, 8, 97.
 - Rutherford, D. R.; Stille, J. K.; Elliott, C. M.; Reichert, V. R. *Macromolecules* 1992, 25, 2294.
 - Havens, S. J. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 3011.
 - Park, Y. T.; Chiesel, N.; Economy, J. *Mol. Cryst. Liq. Cryst.* 1994, 247, 351.
 - Rutherford, D. R.; Stille, J. K. *Macromolecules* 1988, 21, 3530.
 - Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Chapman and Hall Ltd.: London, 1975.
 - Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. In *ACS Symposium Series 282*; Harris, F. W., Spinelli, H. J., Eds.; American Chemical Society: Washington, D.C., 1985, pp 63-79.

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

Nam Hee Kim, Hwan Jin Yeo, and Jong Hwa Jeong*

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

Received February 27, 1996

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.

