

Preparation and Characterization of $WCl_2(Ph_2PCH_2CH_2CH_2CH_2O)_2$

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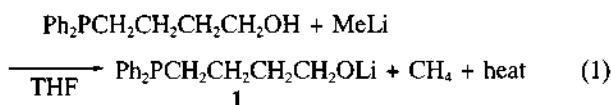
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The use of bidentate tertiary phosphine ligand in organometallic chemistry and catalysis is important on stereochemical control of transition metal complexes.¹ While a bidentate alkoxo-phosphine ligand is expected to give interesting metal complexes which exhibit unusual bonding and novel reactivity owing to "hard" and small size of oxygen atom, not many examples of alkoxo-phosphine ligands are found in the literature. One example is the *O*-metallation product of 2-alkoxy phenylphosphine by the reaction of $[Pt(PBu'_2C_6H_4OR)_2Cl_2]$ in a polar solvent.^{2,3} In this case, a bidentate alkoxo-phosphine ligand has limited synthetic usage due to selective conditions for metallation such as the nature of solvent, steric requirement of coordinated phosphines in the metal complex. To investigate an affinity of a bidentate alkoxophosphine ligand to a transition metal center, we prepared the potential bidentate ligand, $Ph_2PCH_2CH_2CH_2CH_2OLi$ (**1**) by simple lithiation of the corresponding alcohol, diphenyl-4-hydroxybutylphosphine. The reaction of **1** with $WCl_4(PPh_3)_2$ led to the formation of $WCl_2(Ph_2PCH_2CH_2CH_2CH_2O)_2$ (**2**) which exhibited catalytic activity toward the ring opening metathesis polymerization (ROMP) of strained alkenes.

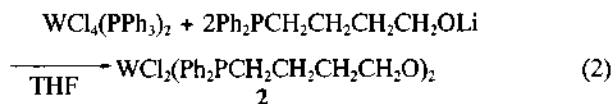
Results and Discussion

Synthesis of 1. Diphenyl-4-hydroxybutylphosphine was prepared according to the literature method⁴ and the bidentate ligand, $Ph_2PCH_2CH_2CH_2CH_2OLi$ was easily obtained by a lithiation of diphenyl-4-hydroxybutylphosphine. The yield of diphenyl-4-lithiobutoxide phosphine, **1** was quantitative when 1.5M of MeLi in diethyl ether was used.



The identification of **1** was carried out by IR spectroscopy and ¹H NMR. The infrared spectrum showed disappearance of OH stretching, previously located at 3412 cm⁻¹ in the corresponding alcohol. In the ¹H NMR spectrum of **1**, the proton bound to oxygen was not appeared, and the other protons in **1** were appeared at 7.1 and 6.7 ppm for phenyl protons, 3.6 ppm for -OCH₂- protons, 2.9 ppm for -CH₂P- protons, 2.6 and 2.3 ppm for remaining -CH₂CH₂- protons.

Synthesis and Characterization of 2. The starting material, $WCl_4(PPh_3)_2$ was prepared by the conventional method.⁵ The preparation of $WCl_2(Ph_2PCH_2CH_2CH_2CH_2O)_2$ was performed by stoichiometric addition of $Ph_2PCH_2CH_2CH_2CH_2OLi$ to $WCl_4(PPh_3)_2$ in THF under an inert atmosphere of argon using standard Schlenk technique. When this reaction was carried out under N₂ gas instead of Ar gas, the complex **2** was not obtained.



The tungsten complex **2** was characterized by elemental analysis, ¹H, ³¹P{¹H} NMR and IR spectroscopy. The IR spectrum showed absorption peaks of aromatic and aliphatic C-H stretchings in the regions of 2800-3100 cm⁻¹. In the ¹H NMR spectrum, positions of resonances were consistent with characteristic regions as shown in Figure 1. The ³¹P NMR spectrum showed a singlet for the phosphorus atoms. This suggested that phosphines were coordinated to an equivalent position in tungsten.

ROMP of Strained Alkenes by 2. It has been known that WCl_6 , $WOCl_4$ or $W(OR)_2Cl_4$ with cocatalysts such as BuLi, LiAlR₄ or R₃Al formed catalytically active mixtures for ring opening metathesis polymerization (ROMP).⁶⁻¹⁰ To test a reactivity of **2** in ROMP, polymerizations of norbornene (NB) and bicyclo-[2,2,1]-hepta-2-ene-7-spiro-1'-cyclopropane (SNB) were performed. Virtually **2** is identified as an effective catalytic precursor for ROMP. It reacted readily with NB to give polynorbornene when MeLi, *i*-(CH₃)₂-CMgCl or Me₃Al was used as a cocatalyst. Similarly **2** gave easily spiro substituted polynorbornene when Me₃Al was used as a cocatalyst. Other cocatalysts such as MeLi or *i*-(CH₃)₂CMgCl was less effective than Me₃Al in the case of SNB monomer. Characterization of polymers was carried out by ¹H NMR spectroscopy. In the ¹H NMR spectrum of the polymer made from NB by a mixture of **2** and AlMe₃, olefinic protons appeared at 5.23 and 5.36 ppm with relative intensities of 1 to 1 assignable to protons bound to *trans* and *cis* double bonds in the polymer chain, respectively. In the ¹H NMR spectrum of the polymer derived from SNB, protons bound to *trans* and *cis* double bonds appeared at 4.97 and 5.13 ppm with relative intensities of 2 to 1,

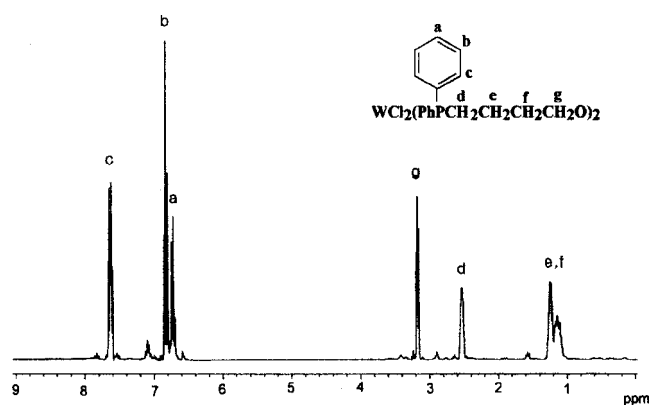


Figure 1. The ¹H NMR spectrum of $WCl_2(Ph_2PCH_2CH_2CH_2CH_2O)_2$ in C_6D_6 .

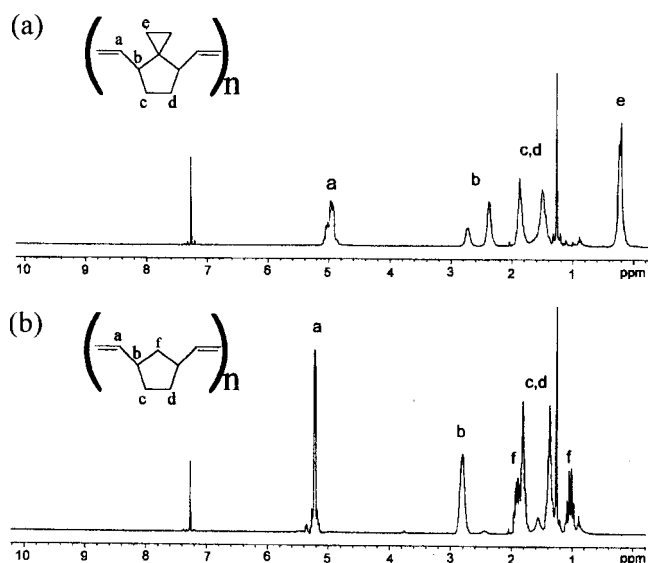


Figure 2(a). The ^1H NMR Spectrum of polymer made from SNB by a mixture of **2** and AlMe_3 in CDCl_3 . (b) The ^1H NMR Spectrum of polymer made from NB by a mixture of WCl_6 and AlMe_3 in CDCl_3 .

respectively. Protons of spiro group were observed in the range of ca. 0.2 ppm. Assignment of other proton resonances were shown in Figure 2 for comparison with the ^1H NMR spectrum of polynorbornene which was obtained by the reaction of a mixture of WCl_6 and AlMe_3 with norbornene. Polymerization by a mixture of $\text{WCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2$ and AlMe_3 gave the polymer chain which contained both cis and trans double bonds. This suggests that the complex $\text{WCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2$ would give different stereo isomers with functionalized strained alkenes contrasting classical catalyst systems such as WCl_6 , AlMe_3 and ReCl_5 , AlMe_3 . Further studies including the effect of cocatalyst and functionalized strained alkene monomers on stereoselectivity by using **2** are in progress.

Experimental Section

General Methods. All manipulations were carried out under a dry Ar and N_2 atmosphere using either Schlenk techniques or a dry box equipped with purification system. Solvents were distilled from $\text{Na}/\text{Ph}_2\text{CO}$ immediately before use. Sealing of NMR tube was performed by a Vacuum Line. Solutions were transferred by the use of a nitrogen flushed syringe, or stainless steel cannulae. Deuterated solvents were degassed via the freeze-thaw method.

Synthesis of the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OLi}$ (1**).** A tetrahydrofuran solution of 29.8 g (0.135 mole) of diphenylchlorophosphine was added dropwise under argon with stirring to a slurry of 100 mL of purified tetrahydrofuran and 3.3 g (0.135 mole) of magnesium ribbon. Reaction occurred immediately. The temperature rose to 68 $^\circ\text{C}$, and the solvent was refluxed. After 4 h of reaction, all of the magnesium

was reacted. When the mixture was cooled, water was added. The organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent left a thick oil of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ which was vacuum distilled at 170 $^\circ\text{C}/0.16$ mmHg (29.0 g, 83.0%). This product was desolved in 100 mL of purified tetrahydrofuran and MeLi was added to this solution. This solution was evaporated for removal of solvent, dried *in vacuo* for 8 h. ^1H NMR (250 MHz, C_6D_6) δ 7.1 (m), 6.7 (m), 3.6 (m), 2.9 (m), 2.6 (m), 2.3 (m). IR (KBr, cm^{-1}) 3068.9 (s), 2922.3 (s), 2808.5 (s), 2706.3 (s), 1957.9 (w), 1479.5 (s), 1433.2 (s), 1093.7 (s), 679.0 (s).

Preparation of $\text{WCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2$ (**2**).

Under Ar atmosphere a suspension of $\text{WCl}_4(\text{PPh}_3)_2$ (2.0 g, 2.4 mmol) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OLi}$ (1.24 g, 4.8 mmol) in THF (50 mL) was vigorously stirred at room temperature for 2 h. The solution was filtered through glass filter. The filtrate was concentrated to ca. 20 mL and cooled to -30 $^\circ\text{C}$ to give powder product. The light green product was filtered, washed with cooled THF (2×10 mL), dried *in vacuo* (0.89 g, 48.4%). ^{31}P NMR (C_6D_6) δ -18.0 (s). IR (KBr, cm^{-1}) 3051.6 (m), 2926.2 (m), 2862.5 (m), 1800-2000 (w), 1433.2 (s), 1358.0 (s), 1068.6 (s) 696.3 (s), 744.6 (s). Anal. Calcd. for $\text{C}_{32}\text{H}_{36}\text{Cl}_2\text{P}_2\text{O}_2$: C, 50.0; H, 4.7. Found C, 50.2; H, 4.8.

General Polymerization Procedure for the NB or SNB with **2.** In a nitrogen-filled glovebox the monomer was dissolved in THF and a small amount of WCl_6 or **2** was added. Polymerization was initiated by dropwise addition of MeLi , AlMe_3 or $(\text{CH}_3)_2\text{CHMgCl}$. After polymerization was finished, polymers were precipitated by addition of acetone (10 mL) and dried *in vacuo*. In a typical scale of these reactions 1 g of monomer was used.

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