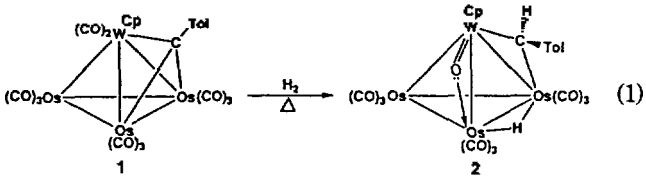
such that W-O(1)=1.79(2) Å, Os(3)-O(1)=2.13(2) Å, and <W-O(1)-Os(3)=95.9(7)°, which reveals the typical unsymmetrical edge-bridging *oxo* ligand. The presence of analogous W=O:→Os bonding has been found previously in μ-*oxo* tungsten complexes [W=O(av)=1.79 Å and Os-O(av)=2.16 Å] such as $CpWOs_3(CO)_9(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$,[11] *anti*-$CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)(\mu\text{-}H)$,[12] $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}C=CHTol)(\mu\text{-}H)$,[13] $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2H_2)(\mu\text{-}H)$,[10] $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)(\mu\text{-}Cl)$,[14] $CpWOs_3(CO)_8(PPh_2Me)(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$,[15] and $CpWOs_3(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$.[16]

The μ-alkylidene ligand bridges the W-Os(1) edge, with W-C(1)=2.05(3) Å, Os(1)-C(1)=2.20(2) Å, and <W-C(1)-Os(1)=83.2(9)°. The configuration of C(1) is such that the C(1)-C(2) vector is oriented toward the μ-*oxo* ligand and the triangular W-Os(1)-Os(3) face. This configuration positions the Tol group *syn* to the W-Os(1)-Os(3) triangular face which is associated with three edge-bridging groups. The *syn* configuration of **2** adopted by the μ-alkylidene ligand places the bulky Cp and Tol moieties apart and avoids their steric congestion.[7]

All other features of the molecular geometry are within the expected range. Individual Os-CO distances range from 1.74(5) through 1.95(3) Å, C-O bond lengths range from 1.09 (3) through 1.28(5) Å and <Os-C-O angles are in the range 169(3)-180(1)°. Tungsten-carbon (Cp) distances vary from 2.29 (3) through 2.46(3) Å and carbon-carbon (Cp) distances are in the range 1.31(7)-1.46(7) Å.

In conclusion, the reaction of **1** with dihydrogen produces an unexpected hydrido-*oxo*-alkylidene complex $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHTol)(\mu\text{-}H)$ of *syn*-isomer as shown in Eq. (1). The source of the *oxo* ligand is not known at the moment. The



1 2 (1)

oxo ligand may be derived from a CO ligand by C-O bond scission or from other possible sources (O_2, H_2O, etc.). Note, however, that *oxo*-alkyne complexes $CpWOs_3(CO)_8(\mu\text{-}O)(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}H)$ (R=H, Ph, Tol) were also produced by initial decarbonylation of the alkyne complexes $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu\text{-}H)$ followed by thermolysis at 110℃.[17]

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Supplementary Material Available. Details of the crystallographic study of **2** are available from the authors (I.-H. S.).

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Convenient Method for the Synthesis of Unsymmetric Thioureas from Unreactive Amines Using $Bu_2Sn(OAc)_2$-$SnCl_2$

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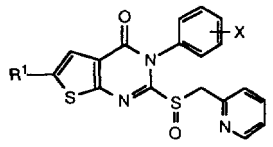
We have been pursuing a synthetic program aimed at the potent H^+/K^+-ATPase inhibitor **1** which could have similar mechanistic behavior in biological system to FDA approved antiulcer agent, omeprazole **2**.[2,3] For the synthesis of com-

Table 1. Dibutyltin Diacetate-Stannous Chloride Catalyzed Coupling of Unreactive Amines with Isothiocyanates

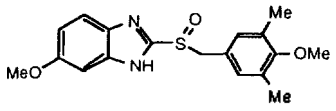
Entry	Compound	R^1	X	Yield, %[a]
1	**4a**	Me	2-F	65
2	**4b**	Et	2-F	58
3	**4c**	Me	3-F	62
4	**4d**	Et	3-F	55
5	**4e**	Me	4-F	61
6	**4f**	Et	4-F	54

[a]purified yield (recrystallized from ether/petroleum ether)

pound **1** we needed various thioureas **4**, crucial intermediates to thienopyrimidinone **3** which serve as precursors to **1**. The most practical method for the preparation of thioureas involve the condensation of amines with corresponding isothiocyanates.[4] However we encountered unexpected problems to couple between amine **5** and aromatic isothiocyanate under the normal conditions. We report herein a novel catalytic system, $Bu_2Sn(OAc)_2$-$SnCl_2$, which was proved to be effective for the reaction between isothiocyanates and unreactive amines.



1



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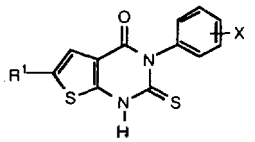
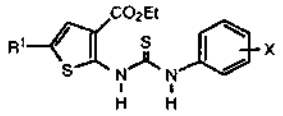
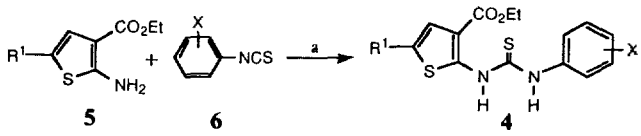


3



4

Initially we started the reaction of amine **5**[5] with 2-fluorophenyl isothiocyanate at various conditions. None of desired thiourea **4**, however, was formed under the various reaction conditions such as refluxing in toluene in the presence of catalytic amounts of *p*-TsOH, Et_3N, or K_2CO_3, presumably due to the unreactivity of amine **5**.[6] Therefore we considered a mean to potentiate the electrophilicity of isothiocyanate by using Lewis acid catalyst, like stannane compounds by virture of strong affinity between sulfur and tin. Indeed we delighted to find that the treatment of amine **5** (R^1=Me) with 2-fluorophenyl isothiocyanate in the persence of catalytic amount of dibutyltin diacetate and stannous chloride in dichloroethane at 80℃ for 6 h afforded thiourea **4** in 65% recrystallized yield. When dibutyltin diacetate or stannous chloride was used alone, the yields were dropped to 38% and 17% respectively. Additional experiments with different



5 **6** **4**

a cat. $Bu_2Sn(OAc)_2$-$SnCl_2$, dichloroethane

substituents were carrid out to afford various thiourea **4** and the results are summarized in Table 1.

In summary, this note describes an effective catalytic system, $Bu_2Sn(OAc)_2$-$SnCl_2$, for the preparation of thioureas from isothiocyanates and unreactive amines and we believe that this catalyst has a potential to be utilized in other reaction system.

Experimental

^{1}H-NMR spectra were taken on a JEOL at 60 MHz and a Varian Gemini-200 at 200 MHz using TMS as internal standard, the chemical shifts being given in δ ppm down field. Mass spectra were measured with Shimadzu QP-1000 spectrometer. IR spectra were recorded on a Shimadzu IR-534 spectrophotometer. Dibutyltin diacetate and stannous chloride were purchased from Alrich Chemical Co.

3-Carboethoxy-2-(2-fluorophenylthioureido)-5-methylthiophene (4a): General Procedure. To a solution of 2-amino-3-carboethoxy-5-methylthiopene (**5**, 1.0 g, 5.4 mmol) in dichloroethane (10 mL) was added $Bu_2Sn(OAc)_2$ (10 mg, 3.0×10^{-2} mmol) and $SnCl_2$ (5.5 mg, 3.0×10^{-2} mmol) followed by 2-fluorophenylisothiocyanate (0.85 g, 5.5 mmol) in dichloroethane (2 *ml*) at 20℃. The resulting reaction mixture was allowed to proceed for 1 h at 20℃ and then was heated at 80℃ for 6 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (10 mL×3). The combined organic layers were washed with water (5 mL), brine (15 mL), dried over anhyrous $MgSO_4$, and then concentrated *in vacuo* to afford crude product which was recrystallized from ether and petroleum ether (1 : 1) to provide pure product **4a** (1.2 g 3.5 mmol, 65%) as a faint yellow shiny crystal : mp. 152-154℃ ; IR (KBr) 3383, 3122, 1659, 1534, 1271 cm^{-1}; mass spectra (EI) m/z 338 (M^+, 15.7), 259 (5.4), 185 (64.8), 156 (7.8), 139 (100); ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, J=6.5 Hz, 3H), 2.35 (s, 3H), 4.10 (q, J=6.5 Hz, 2H), 6.83 (s, 1H), 7.14-7.72 (m, 6H). By the same procedure for the preparatio of **4a**, the following compounds were obtained. **4b**; mp. 141-142℃ ; mass spectra (EI) m/z 352 (M^+); ^{1}H-NMR ($CDCl_3$) δ 1.24 (t, J=7.0 Hz, 6H), 2.68 (q, J=7.0 Hz, 2H), 4.21 (q, J=7.0 Hz, 2H), 6.90 (s, 1H), 7.14-7.72 (m, 6H). **4c**: mp. 173-175℃ ; mass spectra (EI) m/z 338 (M^+); ^{1}H-NMR ($CDCl_3$) δ 1.27 (t, J=6.5 Hz, 3H), 2.35 (s, 3H), 4.15 (q, J=6.5 Hz, 2H), 6.83 (s, 1H), 7.11-7.52 (m, 4H), 7.92 (br. s, 2H). **4d**: mp. 152-154℃ ; mass spectra (EI) m/z 352 (M^+); ^{1}H-NMR ($CDCl_3$) δ 1.24 (t, J=7.0 Hz, 6H), 2.69 (q, J=7.0 Hz, 2H), 4.18 (q, J=7.0 Hz, 2H), 6.84 (s, 1H), 7.01-7.39 (m, 5H), 8.09 (br. s, 1H). **4e**: mp. 49-50℃ ; mass spectra (EI) m/z 338 (M^+); ^{1}H-NMR ($CDCl_3$) δ 1.23 (t, J=7.0 Hz, 3H), 2.34 (s, 3H), 4.12 (q, J=7.0 Hz, 2H), 6.81 (s, 1H), 7.10-7.41 (m, 4H), 7.92 (br. s, 2H). **4f**: mp. 178-180℃ ; mass spectra (EI) m/z 352 (M^+); ^{1}H-NMR ($CDCl_3$) δ 1.29 (t, J=7.0 Hz, 6H), 2.69 (q, J=7.0 Hz, 2H), 4.12 (q, J=7.0 Hz, 2H), 6.81 (s, 1H), 7.05-7.54 (m, 5H), 8.32 (br. s, 1H).

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