



Title	Lewis Acidic Catalysis of Silyl Cyanometallates in Transformations of Phenol and Aniline Derivatives [an abstract of dissertation and a summary of dissertation review]
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## 学位論文内容の要旨

博士の専攻分野の名称      博士    (工学)                      氏名    ECE   Hamdiye

### 学位論文題名

Lewis Acidic Catalysis of Silyl Cyanometallates in Transformations of Phenol and Aniline Derivatives  
(フェノールおよびアニリン誘導体変換反応におけるシリルシアノメタラートの Lewis 酸触媒作用)

Most stable organosilicon compounds, such as tetraalkylsilanes and tetraalkoxysilanes, are neutral, and the Lewis acidity of these compounds is too weak as a catalyst for activation of the organic reagents. However, when one of the four substituents on silicon is changed to Lewis base, such as triflate (OTf) or iodide (I) ion, they become Lewis acids bearing one coordination site. The strength of Lewis acidity mainly depends on the features of the counter anions. Silyl Lewis acids (SLAs) that classified as neutral and cationic have studied for decades. They have shown many advantages for their use over other metal-centered activators and metal halides made them to be chosen as catalysts for many organic reactions like aldol-type reactions, ring constructions, and allylations.

Recently, a new approach for the preparation of cationic SLAs has been reported by Ohkuma, Yurino, and coworkers, that is, silyl cyanometallate complexes formed *in situ* from transition metal salts ( $\text{MX}_n$ ) and an excess amount of trimethylsilyl cyanide (TMSCN). The reversible property of these complexes is proposed to appropriately control the intensity of Lewis acidity. This protocol was successfully applied to allylic isocyanation using allylic phosphate as an electrophile. The ate complexes  $(\text{TMS})[\text{Pd}(\text{CN})_3]$  and/or  $(\text{TMS})_2[\text{Pd}(\text{CN})_4]$  were generated *in situ* from  $\text{Pd}(\text{OAc})_2$  and TMSCN, and these served as both Lewis acids activating allylic phosphates and *N*-nucleophiles of cyanide ( $\text{CN}^-$ ). In a similar manner, the combination of  $\text{Ag}_2\text{O}$  and TMSCN effectively catalyzed the benzylic isocyanation. In this case,  $(\text{TMS})[\text{Ag}(\text{CN})_2]$  is the active species. The author expected that the reversibly formed silyl cyanometallates show unique properties in a variety of Lewis acid-catalyzed reactions other than isocyanations, such as Friedel–Crafts-type substitutions and some oxidations.

This thesis consists of three chapters and the background of this research was described on a general introduction.

Chapter 1: The protocol of Lewis acidic catalysis of silyl cyanometallates has successfully applied to the Friedel–Crafts-type allylation of allylic phosphates and phenol derivatives as nucleophiles. The use of

combined catalyst systems, AgTFA/TMSCN and Pd(OAc)<sub>2</sub>/TMSCN, afforded the *C*-allylated products in high yield. It was found that the AgTFA/TMSCN combination is the suitable catalytic system for selective formation of *para*-allylated anisoles. The Pd(OAc)<sub>2</sub>/TMSCN system worked efficiently for the *para*-selective allylation of phenols. Reactivity of the allylation was influenced by the electronic properties of both nucleophile and electrophile. The reaction of a 1:1 mixture of cinnamyl and simple allyl phosphates exclusively produced the cinnamyl-substituted compound.

Chapter 2: The Pd(OAc)<sub>2</sub>/TMSCN combined system efficiently catalyzed Friedel–Crafts-type cyclization of diethylphosphates derived from *N*-arylmandelamides. This is the first successful example of the catalytic reaction. Wide varieties of the 3-aryloxindole products were obtained in nearly quantitative yield. Substitution of methyl, isopropyl, *tert*-butyl, and phenyl groups on the nitrogen was allowed with little influence on the product yield. *N*-Allyl and *N*-benzyl substituents were not injured by the Pd complexes. Methyl, methoxy, and halide groups were successfully introduced on the mandelic as well as the aniline phenyl rings of substrates. The mandelic phenyl ring could be replaced with naphthyl and thienyl groups, affording the cyclized products quantitatively. When the reaction was conducted with *N,N*-dibenzylmandelamide as a substrate, the benzo-fused  $\delta$ -lactam was obtained in a quantitative yield. Application of the oxindole product to the C3-substitution reactions afforded the 3,3-diaryloxindoles with two different aromatic rings.

Chapter 3: The silyl cyanoargentate catalyzed oxidative cyanomethylation of *N*-alkylanilines with TMSCN and nitromethane mediated by benzotrifluoride to afford the *N*-alkyl-*N*-cyanomethylaniline predominantly. The three-component coupling reaction proceeded under air. The yield was significantly reduced in the absence of benzotrifluoride. It suggested that benzotrifluoride promoted the oxidative process. The reaction did not undergo through a traditional oxidative Strecker-type reaction of tertiary amine. The use of nitromethane was crucial. No desired product was obtained with acetonitrile instead of nitromethane.