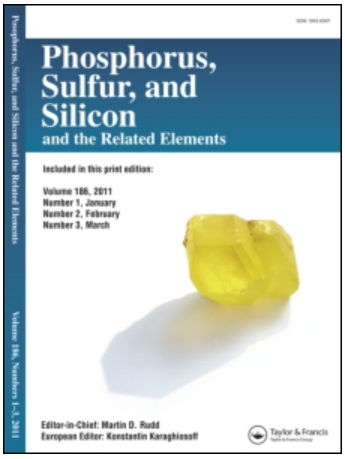

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Syntheses of Polythioethers Tethered with Bulky Aryl Groups and Their Complexation with Late-Transition Metals

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*New types of o-phenylene-bridged polythioethers tethered with extremely bulky aryl groups at their terminal sulfur atoms, such as TbtS(o-Phen)S(o-Phen)S(o-Phen)STbt (**1**) and TbtS(o-Phen)S(o-Phen)SS(o-Phen)S(o-Phen)STbt (**2**) (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, o-Phen = o-phenylene), were synthesized and subjected to the complexation with several kinds of late-transition metals. In the case of polythioether **1**, the reaction with $RhCl_3 \cdot 3H_2O$ in benzene/EtOH resulted in the formation of a unique bimetallic complex, in which a part of ligand **1** is lost and the resulting sulfur atom is directly bound to the other Rh metal center. Interestingly, similar treatment of **1** with $IrCl_3 \cdot 3H_2O$ afforded ethyl-coordinated mononuclear Ir complex. Furthermore, **1** underwent complexation with Na_2PdCl_4 in EtOH to give the corresponding square planar dichloropalladium complex coordinated with two inner sulfur atoms of **1**, while the S_6-ligand **2** reacted with excess of $Pd(PPh_3)_4$ in benzene to afford a quite interesting trinuclear Pd complex* via *multi-step metal insertion reactions.*

Keywords Bimetallic complex; complexation; coordination; mononuclear complex; polythioethers; transition metals

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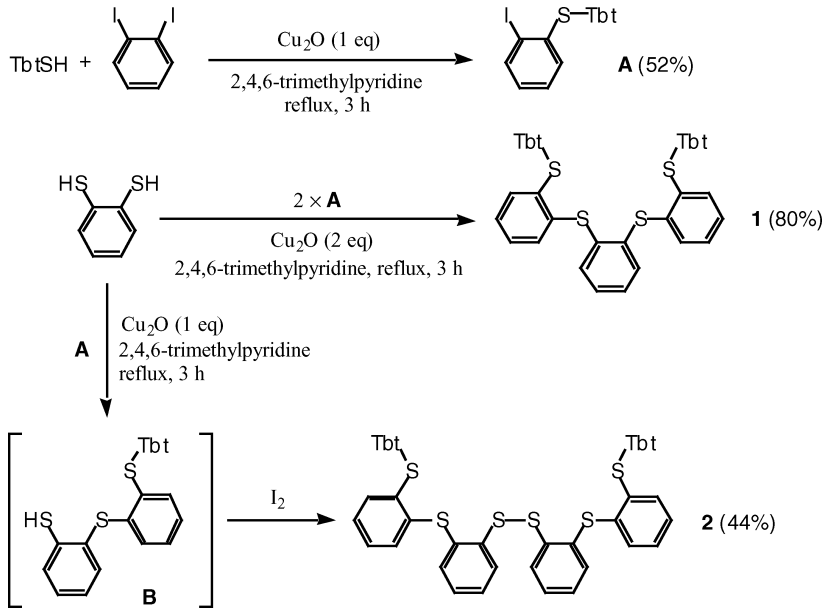
INTRODUCTION

Thiacrown ethers are well-known host compounds capable of complexation with a variety of transition metals.[1] Although their high ability at metal recognition is achieved as a result of size selectivity, the rigidity of the ring (crown) structure sometimes makes it difficult to coordinate to a metal center as a three-dimensional multidentate ligand. On the other hand, as an extension of our study on the sterically crowded organosulfur compounds, we have recently prepared some new polythioethers tethered with bulky aryl groups (**1** and **2**).[2] We present here the synthesis and structures of **1** and **2** together with their coordination ability toward some late-transition metals.

RESULTS AND DISCUSSION

As a terminal protecting group, we introduced an extremely bulky aryl group, that is, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), which has been successfully applied to the kinetic stabilization of a variety of highly reactive species of heavier elements.[3]

Polythioether **1** was readily prepared by the treatment of *o*-benzenedithiol with 2-I-C_6H_4STbt (**A**; 2 equivalents (eq.)) in the presence of Cu_2O (2 eq) and 2,4,6-trimethylpyridine in 80% yield (Scheme 1).[4]

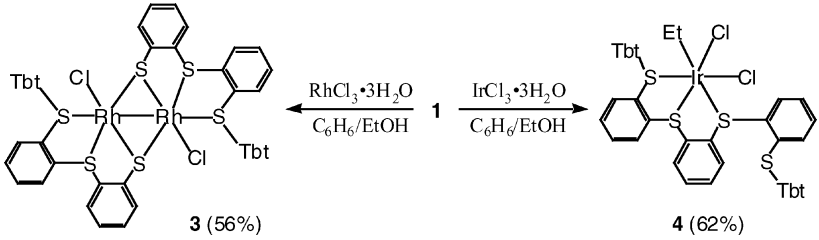


SCHEME 1

On the other hand, S_6-ligand **2** was synthesized in 44% yield by the reaction of *o*-benzenedithiol with equimolar amounts of thiol **A** and Cu_2O under similar conditions, followed by the oxidative coupling reactions of the resulting thiol intermediate **B** with iodine (Scheme 1).

Both polythioethers **1** and **2** were isolated as stable, colorless crystals, and their molecular structures were confirmed with ^1H NMR, ^3C NMR, and MS spectra. Crystallographic analysis of **1** and **2** showed that they have extended structures with some intramolecular interactions among the sulfur atoms. In addition, it was expected that they might have enough flexibility for the complexation toward transition metals with their sulfide moieties as a multidentate ligand.

First, we have examined the complexation of polythioether **1** with group 9 metal trichlorides. The reaction of **1** with $RhCl_3 \cdot 3H_2O$ in benzene/EtOH under reflux for 24 h resulted in the formation of a unique bimetallic complex **3** as a main product (56%), in which a part of ligand **1** is lost and the resulting sulfur atom is directly bound to the other Rh metal center (Scheme 2). In this case, TbtSPh was isolated as a byproduct in 71% yield, whereas similar treatment of **1** with $IrCl_3 \cdot 3H_2O$ afforded a mononuclear Ir complex **4** in 62% yield (Scheme 2). The molecular structures of the newly obtained complexes **3** and **4** were determined by X-ray crystallographic analysis, which revealed the dirhodium core structure for **3** bridged with two μ-sulfur ligands and the octahedral Ir center for **4** coordinated with three sulfur and two chlorine atoms together with an ethyl ligand. In the ball-and-stick model drawing of complex **4** (Figure 1), one can see the unique coordination mode of ligand **1** toward the ethyl-substituted Ir center.



3 (56%) **4** (62%)

SCHEME 2

It is of great interest that the final products of the complexation of **1** with $MCl_3 \cdot 3H_2O$ (M = Rh, Ir) are drastically different from each other although **1** was mixed with these metal trichlorides under similar reaction conditions. The formation of such type of an ethyl-coordinated iridium complex, *trans*-$[IrCl(Et)L1]^+$, has previously been reported in the

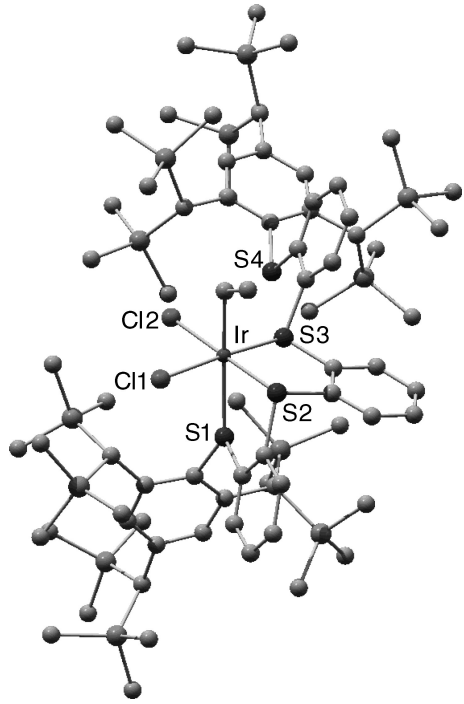
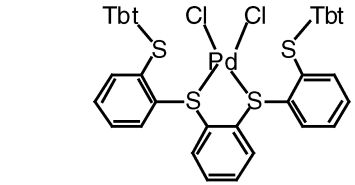


FIGURE 1 Molecular structure of **4**.

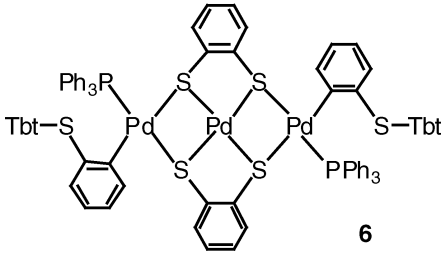
reaction of a pyridine-containing tetraazamacrocycle, 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L1) with $IrCl_3 \cdot 3H_2O$ in refluxing aqueous ethanolic solution.[5] The formation of dirhodium complex **3** together with TbtSPh in moderate yields strongly implies the intermediacy of a mononuclear rhodium complex, which may undergo some intramolecular C—S activation.

Furthermore, polythioether **1** was found to undergo complexation with Na_2PdCl_4 in refluxing EtOH for 1 h to give the corresponding dichloropalladium complex **5** in an almost quantitative yield (Scheme 3). The X-ray crystallographic analysis of **5** showed that the dichloropalladium center was coordinated to the inner two sulfur atoms of **1** with an almost square planar geometry, while the terminal sulfide moieties (TbtS units) were oriented in the axial positions with weak attractive interaction between the sulfur atoms and the Pd center.

Although the reaction product of S_6-ligand **2** with Na_2PdCl_4 has not been characterized yet because of the difficulty in its separation and purification, the reaction of **2** with 3 equivalent molar amounts of $Pd(PPh_3)_4$ in benzene was examined at room temperature to



5



6

SCHEME 3

afford a quite interesting trinuclear Pd complex **6** in 58% isolated yield (Scheme 3).

Further investigation of the formation mechanism of the newly obtained complexes **3**–**6** and the complexation reactions of polythioether ligands **1** and **2** with other transition metals are currently in progress.

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