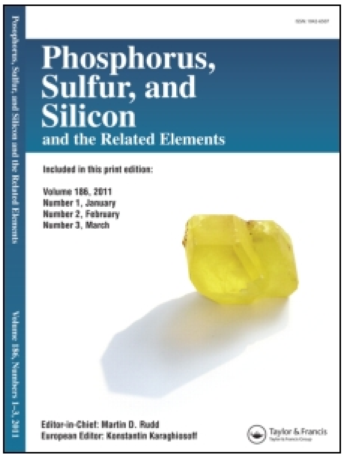

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Synthesis of Novel Platinum Dichalcogenido-Complexes by Taking Advantage of Bulky Phosphine Ligands

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SYNTHESIS OF NOVEL PLATINUM DICHALCOGENIDO-COMPLEXES BY TAKING ADVANTAGE OF BULKY PHOSPHINE LIGANDS

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The first stable disulfido and diselenido complexes of platinum-bearing bulky phosphine ligands were synthesized by the reaction of the corresponding zerovalent platinum complexes with elemental sulfur and selenium, respectively. The molecular structures of these complexes were determined by spectral data, elemental analysis, and X-Ray crystallographic analysis.

Keywords: Bulky phosphine ligand; platinum disulfido complex; platinum diselenido complex; three-membered ring

INTRODUCTION

Recently, there has been an increasing interest in the structure and reactivity of transition metal–chalcogen complexes.[1] However, the chemistry of mononuclear platinum chalcogenido-complexes remained unexplored. We have already reported the synthesis of tetrachalcogenametallolanes containing a heavier group 14 element by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.[2] These results prompted us to examine the synthesis of platinum chalcogenido complexes having bulky ligands. Here, we report the synthesis of the first platinum dichalcogenido-complexes **1a**,**b** having a PtX_2 ($X = S,Se$) ring by taking advantage of phosphine ligands bearing an extremely bulky aryl substituent, i.e., Tbt or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group.

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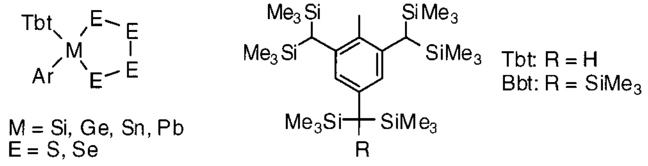
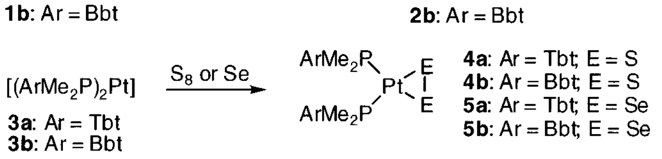


SCHEME 1

RESULTS AND DISCUSSION

Bulky phosphine ligands **1a**,**b** were prepared by the treatment of TbtLi or BbtLi with PCl_3, followed by the addition of MeLi (2 eq). The reaction of 2 molar amounts of phosphines **1a**,**b** with K_2PtCl_4 gave the corresponding platinum dichloride complexes **2a**,**b**. Complexes **2a**,**b** were reduced by an excess of lithium naphthalenide in THF to give the corresponding zerovalent platinum complexes **3a**,**b**, and the successive addition of elemental sulfur or selenium resulted in the formation of the corresponding platinum dichalcogenido-complexes **4a**,**b** and **5a**,**b** in moderate yields. To our knowledge, no disulfido and diselenido complexes of platinum has been reported so far, though platinum dioxygen complexes have been extensively studied.[3] These complexes are the first examples of complexes having a three-membered PtE_2 (E = S, Se) ring system.



SCHEME 2

These new platinum complexes **4a**,**b** and **5a**,**b** were characterized by NMR spectrometry, high resolution mass spectrometry, and elemental analysis, and the molecular structures of **4b** and **5b** were finally determined by X-ray crystallographic analysis (for compound **4b**, see Figure 1). In both cases of **4b** and **5b**, the platinum atom had square

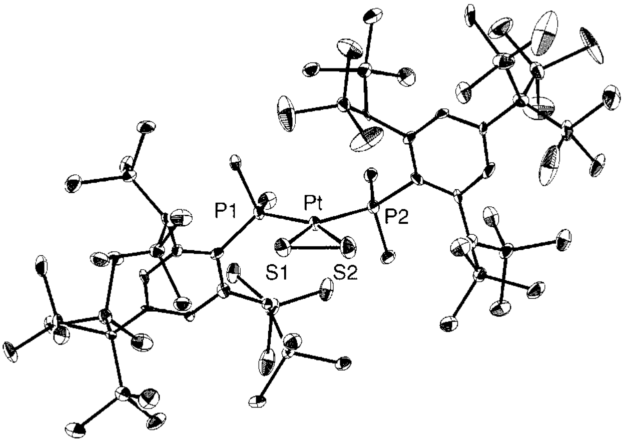
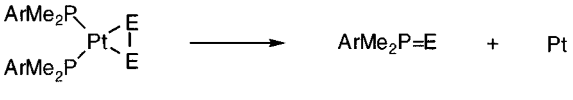


FIGURE 1 ORTEP drawing of **4b** with thermal ellipsoids (50% probability).

planar structure, and the Bbt groups were in trans positions with regard to the PtE_2 (E = S, Se) plane. The lengths of Pt—E and E—E bonds [Pt—S: 2.348(3) and 2.337(3) Å, S—S: 2.077(3) Å for **4b** (E = S); Pt—Se: 2.4491(10) and 2.4658(9) Å, Se—Se: 2.3363(11) Å for **5b** (E = Se)] are similar to those of platinum tetrachalcogenido complexes (Pt—S: 2.364 (av) Å, S—S: 2.042 (av) Å for $(Ph_3P)_2PtS_4$;[4] Pt—Se: 2.457 (av) Å, Se—Se: 2.331 (av) Å for $(dppe)PtSe_4$ [dppe = bis(diphenylphosphino)ethane]),[5] supporting the three-membered ring structure of the PtE_2 moieties.

Although compounds **4a**,**b** and **5a**,**b** are obtained as air-stable in the solid state, they decomposed in solution to the corresponding phosphine chalcogenide and metallic platinum standing at room temperature for several days.



4a,b, 5a,b

SCHEME 3

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