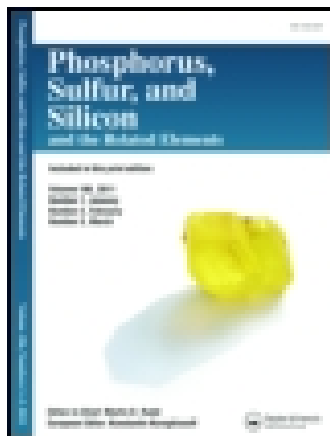


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Synthesis of Novel Platinum Dichalcogenido-Complexes by Taking Advantage of Bulky Phosphine Ligands

Kazuto Nagata ^a, Nobuhiro Takeda ^a & Norihiro Tokitoh ^a

^a Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan

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

Kazuto Nagata, Nobuhiro Takeda, and Norihiro Tokitoh
Institute for Chemical Research, Kyoto University, Gokasho, Uji,
Kyoto 611-0011, Japan

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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 tetrachalcogenametallophanes 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 PtX₂ (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.

Address correspondence to N. Tokitoh, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. E-mail: tokitoh@boc.kuier-kyoto-u.ac.jp



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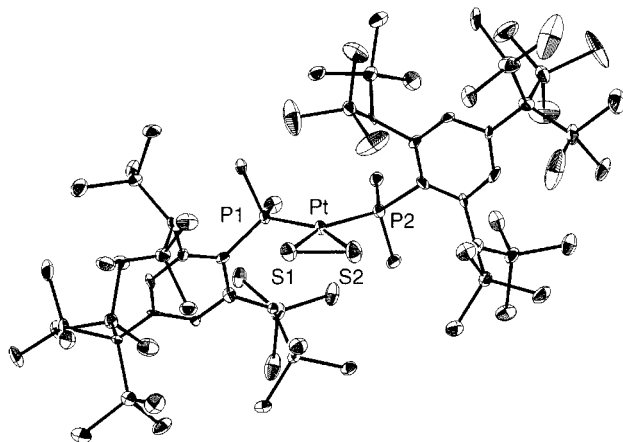
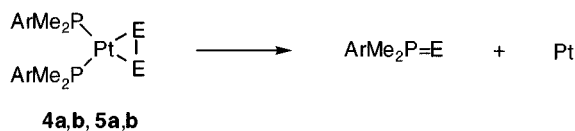


FIGURE 1 ORTEP drawing of **4b** with thermal ellipsoids (50% probability).

planar structure, and the Bbt groups were in trans positions with regard to the PtE_2 ($\text{E} = \text{S}, \text{Se}$) plane. The lengths of $\text{Pt}-\text{E}$ and $\text{E}-\text{E}$ bonds [$\text{Pt}-\text{S}$: 2.348(3) and 2.337(3) Å, $\text{S}-\text{S}$: 2.077(3) Å for **4b** ($\text{E} = \text{S}$); $\text{Pt}-\text{Se}$: 2.4491(10) and 2.4658(9) Å, $\text{Se}-\text{Se}$: 2.3363(11) Å for **5b** ($\text{E} = \text{Se}$)] are similar to those of platinum tetrachalcogenido complexes ($\text{Pt}-\text{S}$: 2.364 (av) Å, $\text{S}-\text{S}$: 2.042 (av) Å for $(\text{Ph}_3\text{P})_2\text{PtS}_4$;⁴ $\text{Pt}-\text{Se}$: 2.457 (av) Å, $\text{Se}-\text{Se}$: 2.331 (av) Å for $(\text{dppe})\text{PtSe}_4$ [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.



SCHEME 3

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