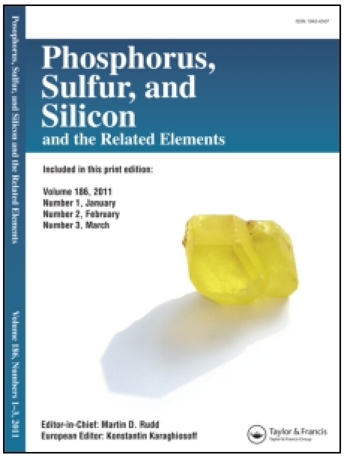


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Preparation, Crystal Structure, And Properties Of Dicationic Bis(Diaryltellurium(IV)) Oxide

Kenji Kobayashi; Nobuo Deguchi; Ernst Horn; Naomichi Furukawa

To cite this Article Kobayashi, Kenji , Deguchi, Nobuo , Horn, Ernst and Furukawa, Naomichi(1998) 'Preparation, Crystal Structure, And Properties Of Dicationic Bis(Diaryltellurium(IV)) Oxide', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 509 — 512

To link to this Article: DOI: 10.1080/10426509808545984

URL: http://dx.doi.org/10.1080/10426509808545984

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 509–512
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

PREPARATION, CRYSTAL STRUCTURE, AND PROPERTIES OF DICATIONIC BIS(DIARYLTELLURIUM(IV)) OXIDE

KENJI KOBAYASHI, NOBUO DEGUCHI, ERNST HORN, and NAOMICHI FURUKAWA
Department of Chemistry and Tsukuba Advanced Research Alliance Center, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

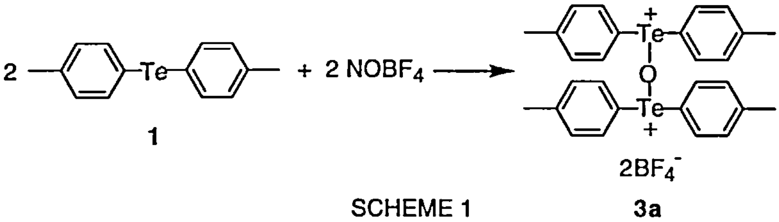
The oxygen atom insertion of nitrogen monoxide or O_2 molecule between tellurium atoms by various chemical oxidation methods of diaryl telluride to produce dicationic bis(diaryltellurium(IV)) oxide is described.

Keywords: diaryl telluride; oxidations; nitrogen monoxide; triflic anhydride; insertions

INTRODUCTION

Formation of σ-bonded dichalcogena dications by intermolecular reaction has received much less attention. As part of our aim to achieve the formation of an intermolecular ditellura dication and multitellurane dications, here we report the preparation, crystal structure, and properties of the dicationic bis(diaryltellurium(IV)) oxide 3 that is apparently produced via the first oxygen atom insertion of nitrogen monoxide or O_2 molecule between tellurium atoms by various chemical oxidation methods of diaryl telluride.[1]

Reaction of Diaryl Telluride with $NOBF_4$

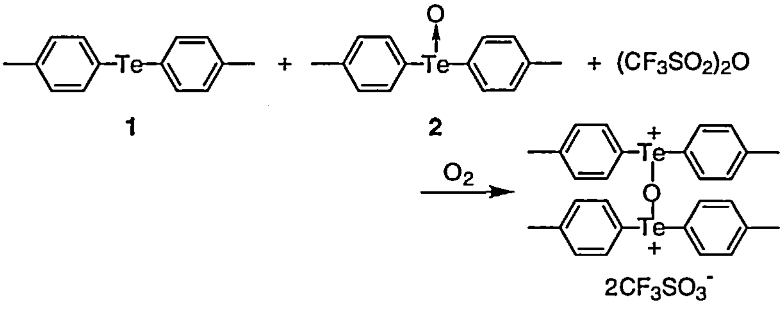


SCHEME 1

Treatment of bis(4-methylphenyl) telluride (**1**) with 1 equiv of $NOBF_4$ in dry CH_2Cl_2-CH_3CN at -40 °C under an Ar atmosphere for 30 min afforded bis[bis(4-methylphenyl)tellurium(IV)] oxide bis(tetrafluoroborate) (**3a**) in quantitative yield (Scheme 1). The ^{125}Te NMR spectrum of **3a** in CD_3CN shows a peak at $\delta = 1301.3$, shifted downfield by 646 ppm relative to **1**. This remarkable downfield shift is characteristic of a cationic species. The FAB-MS spectrum of **3a** exhibits a parent peak at $m/z = 655$ [M^+] (where, $M^+ = (M\text{-}2BF_4^- + F^-)^+$). The compound **3a** reacted with 4 equiv of thiophenol under an Ar atmosphere to give **1** and diphenyl disulfide in quantitative yields, respectively. Treatment of **3a** with aqueous NaOH quantitatively afforded bis(4-methylphenyl) telluroxide (**2**). These results undoubtedly support the formation of **3a** having the dicationic Te-O-Te bond, in which the Te atoms are tri-coordinated.

Bis[(halide)diaryltellurium(IV)] oxides having tetra-coordinate Te atoms are generally prepared by the thermal dehydration of diaryltellurium hydroxy halides and their derivatives. The present reaction is not of this type. It proceeds instantaneously at -40 °C under both anhydrous and anaerobic conditions. The reaction in the presence of 2 equiv of $H_2{}^{18}O$ gave **3a**, the FAB-MS spectrum of which showed no incorporation of ^{18}O atom into **3a**. These results suggest that nitrogen monoxide (NO) which is generated from the redox reaction of **1** with $NOBF_4$ would be a source of the oxygen atom in **3a**. Thus, a radical cation of **1** or the corresponding ditellura dication formed by dimerization would react with NO to give **3a**.

Reaction of a 1:1 Mixture of Diaryl Telluride and Its Telluroxide with Triflic Anhydride



SCHEME 2 **3b**

A similar dicationic bis(diaryltellurium(IV)) oxide ditriflate (**3b**) was quantitatively obtained by the reaction of a 1:1 mixture of **1** and its telluroxide **2** with 1 equiv of triflic anhydride (Tf_2O) in dry CH_3CN at -40 °C to room temperature under an O_2 atmosphere for 1 h (Scheme 2). In solution, the triflate as a counter anion is not expected to be coordinated to the Te atoms, because the chemical shift of **3b** in the

^{125}Te NMR spectrum (1288.4 ppm) is almost the same as that of **3a**. Under an Ar atmosphere, The reaction shown in Scheme 2 afforded no **3b** and, hence, molecular oxygen is essential for the formation of **3b**.

The following mechanism seems to be plausible. The reaction of **2** with Tf_2O may lead to a diaryl(triflate)telluronium salt or diaryltellurium ditriflate which reacts with **1** to afford an intermolecular ditellura dication and two molecules of triflate. The insertion of O_2 into the resulting ditellura dication would produce **3b**.

The crystal structure of **3b** was determined by X-ray diffraction analysis as shown in Figure 1. Molecules of **3b** associate in pairs across a center of symmetry located between the atoms O1 and O1' (where, the primed atoms refer to the respective symmetry related atoms at 1-x,-y,-z). Each of the four counter anions interacts with the Te atoms of the paired dications via their oxygen atoms in the range 2.64-2.98 Å. These contacts are considerably shorter than the sum of van der Waals radii (3.60 Å) of the two elements. Thus, each Te atom has a pseudo octahedral geometry.

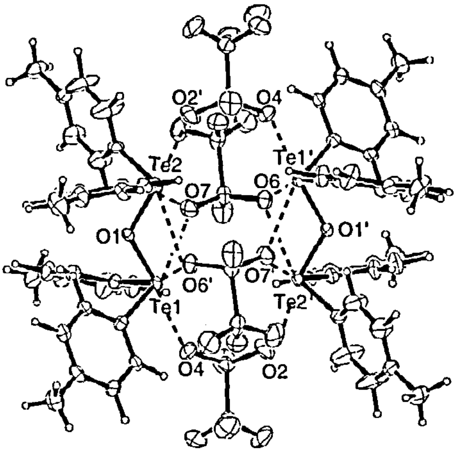


FIGURE 1 X-ray crystal structure of **3b**

Reference

[1] K. Kobayashi, N. Deguchi, E. Horn, N. Furukawa, *Angew. Chem. Int. Ed. Engl.* in press.