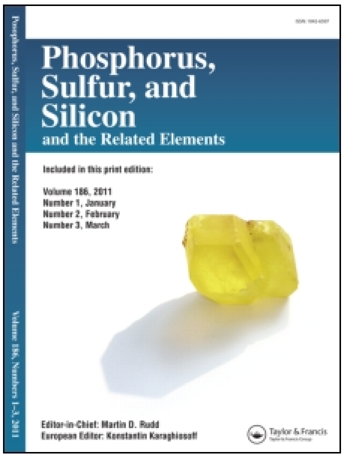

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Carbon Sulfur Double Bonds

Thomas Henkel[a]; Axel Klauck[a]; Konrad Seppelt[a]
[a] Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Berlin, Germany

To cite this Article Henkel, Thomas , Klauck, Axel and Seppelt, Konrad(1994) 'Carbon Sulfur Double Bonds', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 313 — 314

To link to this Article: DOI: 10.1080/10426509408034215

URL: http://dx.doi.org/10.1080/10426509408034215

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 313–314
Reprints available directly from the publisher
Photocopying permitted by license only

Published under license by Gordon and Breach Science Publishers SA
Printed in the United States of America

CARBON SULFUR DOUBLE BONDS

THOMAS HENKEL, AXEL KLAUCK, KONRAD SEPPELT
Institut für Anorganische und Analytische Chemie, Freie Universität
Berlin, D-14195 Berlin, Germany

Abstract. Preparation, properties and structure of cyclopentadienylidene sulfur tetrafluoride (c-H_4C_5=SF_4) and fluorosulfurylmethylidene sulfur difluoride oxide (F-SO_2-CH=SF_2=O) are discussed.

INTRODUCTION

All of the following carbon sulfur double bonds with sulfur in different oxidation states are known by now; >C=S, >C=SR_2 (R = Alkyl, F), >C=S=O, >C=SF_4, >C=SR_2=O (R=Alkyl, F). For a review on the Fluorine substituted species see.[1]

Here we present further discussion on the alkylidene sulfur tetrafluorides (R_2C=SF_4) and alkylidene sulfur difluoride oxides.

1. Cyclopentadienylidene sulfur tetrafluoride, c-C_5H_4=SF_4.

Alkylidene sulfur tetrafluorides are stable, colorless gases or liquids and they have a peculiar structure. The sulfur atom has trigonal bipyramidal geometry, with the carbon atom in an equatorial position. The pairs of fluorine atoms together with the sulfur atom define an axial and an equatorial plane. The carbon substituents are positional in the axial plane. Neither there is rotation around the CS bond nor is there equilibration of the different fluorine atoms on the n.m.r. time scale. These facts together with the bond length of the CS bond (~155 pm) defines the latter as a true double bond. In a deformation electron density measurement of $F_3C(H_3C)C=SF_4$ even an anisotropic electron density of the CS bond could be established.

The question was how c-$H_4C_5=SF_4$ would behave. In case the resonance formula SF_4 would play an important role, free rotation of the CS bond and equilibration of the fluorine atoms should become observable, may be at elevated temperatures. c-$H_4C_5=SF_4$ was obtained by two different routes, and it turned out to be a rigid species. It is made in the last step from SF_5. From this cyclopentadien a thallium and two rhodium complexes have been prepared.

2. Fluorsulfanylmethylidesulfurdifluorideoxide, $F-SO_2-CH=SF_2=O$.

There are very few examples of alkylidenesulfur difluoride oxides known. The best investigated material is $F-CO-CH=SF_2=O$. In the n.m.r. it shows a dynamic behavior because of rotation around the CS and CC bonds, that is strongly temperature dependent. The question is whether $F-SO_2-CH=SF_2=O$ would behave likewise. It is made in two steps starting with $H_2C=SF_4$. In the solid state it has a structure with a cis-planar -HC=S=O group. This is the same geometry that is proposed for $F-CO-CH=SF_2=O$ as the most stable rotamer. However $F-SO_2-CH=SF_2=O$ shows no dymeric behavior. It cannot be said at present if it is a rigid species, or if there is free rotation of the double bond that cannot be frozen in. The CS bond length is the same like in $R_2C=SF_4$.

REFERENCES

1. K. Seppelt, Angew. Chem. 103 (1989) 399; Angew. Chem. Int. Ed. Engl. 30 (1989) 361.