

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### Structures and Reaction Mechanism of Novel Metal-Carbene Complexes Derived from Hypervalent Diazadiselenathiapentalenes

Fujiko Iwasaki; Hideyuki Nishiyama; Noriko Manabe; Masanori Yasui; Noboru Matsumura

**To cite this Article** Iwasaki, Fujiko , Nishiyama, Hideyuki , Manabe, Noriko , Yasui, Masanori and Matsumura, Noboru(1997) 'Structures and Reaction Mechanism of Novel Metal-Carbene Complexes Derived from Hypervalent Diazadiselenathiapentalenes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 429 — 430

**To link to this Article:** DOI: 10.1080/10426509708545582

**URL:** <http://dx.doi.org/10.1080/10426509708545582>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## STRUCTURES AND REACTION MECHANISM OF NOVEL METAL-CARBENE COMPLEXES DERIVED FROM HYPERVALENT DIAZADISELENATHIAPENTALENES

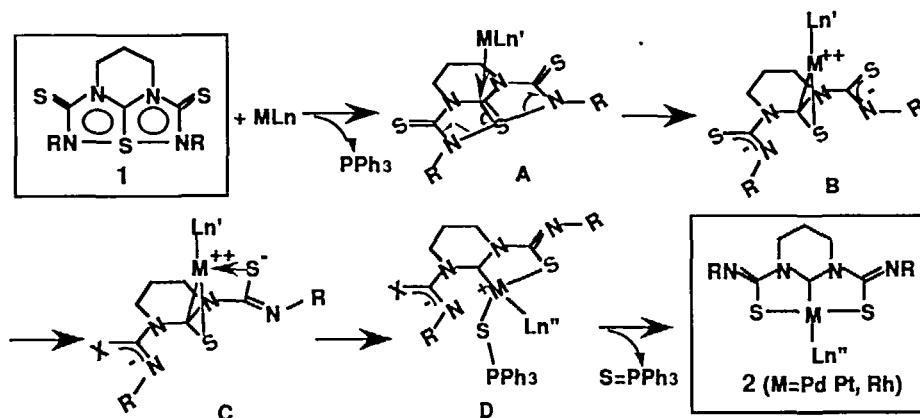
FUJIKO IWASAKI,\* HIDEYUKI NISHIYAMA, NORIKO MANABE, MASANORI YASUI AND NOBORU MATSUMURA†

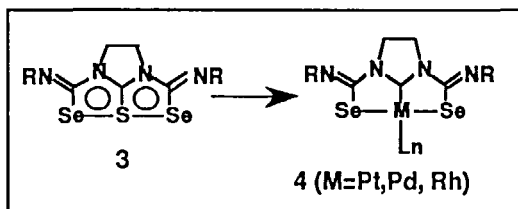
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

†Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

**Abstract** Novel metal-carbene complexes (**4**) with a metallapentalene framework have been obtained from hypervalent diazadiselenathiapentalenes (**3**) by treating with  $\text{Pt}(\text{PPh}_3)_4$ ,  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{RhCl}(\text{PPh}_3)_3$ . X-Ray investigations revealed that the central hypervalent sulfur atom in **3** was substituted by a metal atom to form M-Se bonds in the resultant metallapentalene framework.

Novel metal-carbene complexes (**2**) with a metallapentalene framework have been obtained from hypervalent tetraaza-6a-thiapentalenes (**1**) by treating with  $\text{Pt}(\text{PPh}_3)_4$ ,  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{RhCl}(\text{PPh}_3)_3$ . X-Ray investigations revealed that the central hypervalent sulfur atom in **1** was substituted by a metal atom and that thioamide groups on one or both sides rotated to form metal-sulfur bonds in the resultant metallapentalene framework.[1,2] From the MO calculations on Frontier electron densities of **1** and the structures of these carbene complexes, we proposed the mechanism of the formation of these metal-carbene complexes as shown in the scheme.[3]





This scheme suggests that a similar carbene complex should be obtained from S-S-S or Se-S-Se hypervalent systems instead of N-S-N hypervalent systems. In fact, metal complexes were obtained from diselenathiapentalenes, **3**.

X-ray structure analyses revealed that these complexes were also novel metal-carbene complexes **4** coordinated by Se atoms. The structure of the Pd-complex (**4**) is shown in Fig. 1. In the complexes (**4**), the central sulfur atom of **3** is also substituted by the metal atom to form a square planar configuration like that of **2**. The four coordination sites are occupied by a tridentate ligand containing a diselenapentalene framework and a PPh<sub>3</sub> ligand. The metallapentalene framework is planar. The distances of Pd-Se bonds in the complex (**4**) are 2.414(1) and 2.436(1) Å. These lengths are longer than Pd-S bonds in **2** by the difference of the covalent radii of Se and S. The lengths of Pd-P (2.335(1) Å) and Pd-C (1.974(5) Å) bonds are similar to those of the corresponding bonds of **2**.

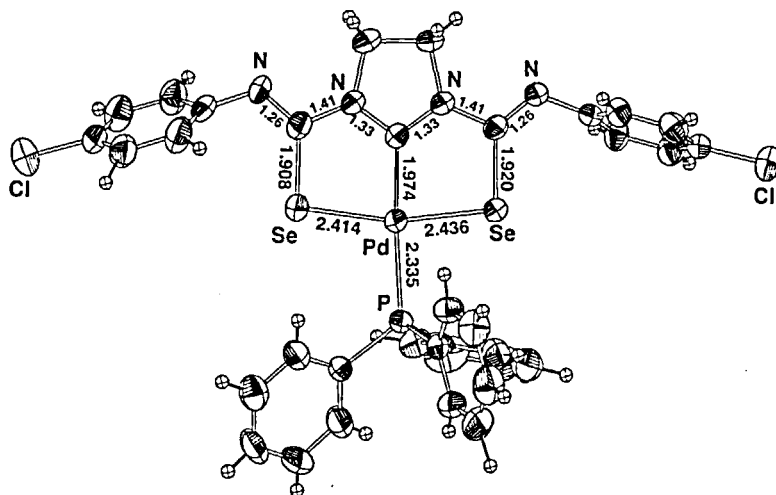


FIGURE 1. Molecular structure the Pd-complex **4**

## REFERENCES

1. N. Matsumura, J. Kawano, N. Fukunishi, H. Inoue, M. Yasui, F. Iwasaki *J. Am. Chem. Soc.*, **117**, 3623-3624 (1995).
2. M. Yasui, S. Yoshida, S. Kakuma, S. Shimamoto, N. Matsumura, H. Inoue, F. Iwasaki *Bull. Chem. Soc. Jpn.*, **69**, to be published. (1996).
3. N. Manabe, H. Nishiyama, S. Shimamoto, M. Yasui, N. Matsumura, H. Inoue, F. Iwasaki *Bull. Chem. Soc. Jpn.*, **69**, to be published. (1996).