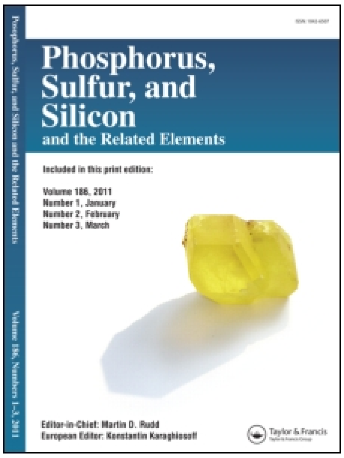


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

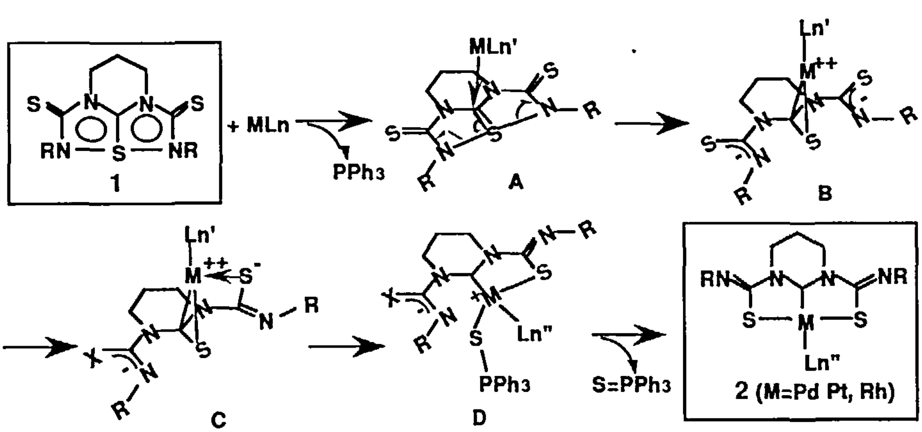
Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 429–430
Reprints available directly from the publisher
Photocopying permitted by license only

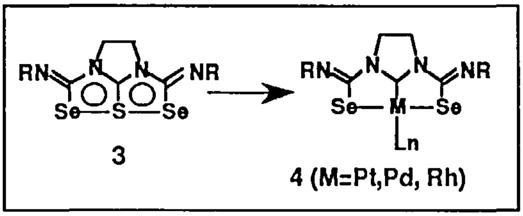
STRUCTURES AND REACTION MECHANISM OF NOVEL METAL-CARBENE COMPLEXES DERIVED FROM HYPERVALENT DIAZADISELENATHIAPENTALENES

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 $Pt(PPh_3)_4$, $Pd(PPh_3)_4$ and $RhCl(PPh_3)_3$. 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 $Pt(PPh_3)_4$, $Pd(PPh_3)_4$ and $RhCl(PPh_3)_3$. 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_3 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**.

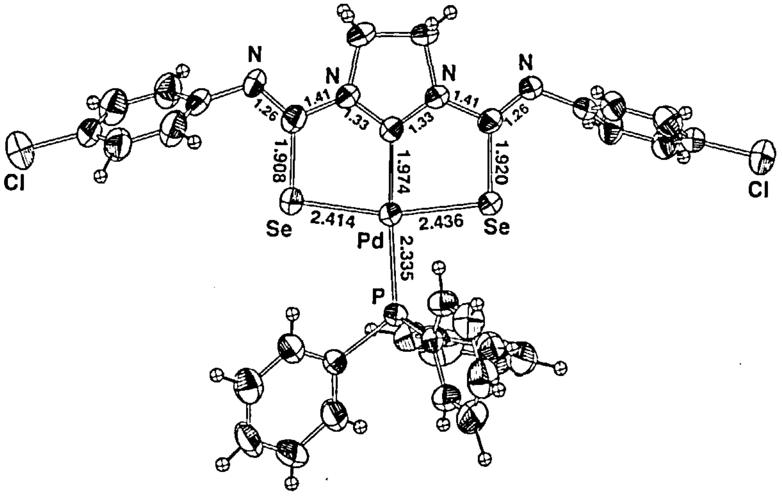


FIGURE 1. Molecular structure the Pd-complex **4**

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. Matsumure, H. Inoue, F. Iwasaki Bull. Chem. Soc. Jpn., 69, to be published. (1996).
3. N. Manabe, H. Nishiyama, S. Shimamoto, M. Yasui, N. Matsumure, H. Inoue, F. Iwasaki Bull. Chem. Soc. Jpn., 69, to be published. (1996).