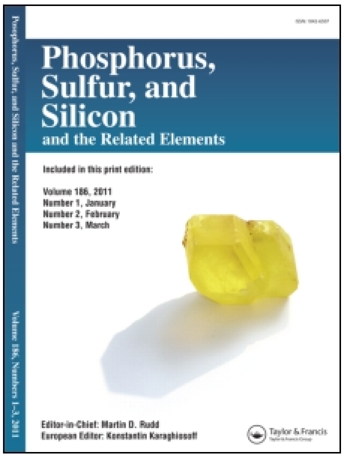


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactivity of a Cationic Phosphenium Complex of Tungsten Containing an Alkyl or a Stannyl Group

Hiroshi Nakazawa; Mitsuru Kishishita; Katsuhiko Miyoshi

To cite this Article Nakazawa, Hiroshi , Kishishita, Mitsuru and Miyoshi, Katsuhiko(1999) 'Reactivity of a Cationic Phosphenium Complex of Tungsten Containing an Alkyl or a Stannyl Group', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 45 — 48

To link to this Article: DOI: 10.1080/10426509908546178

URL: http://dx.doi.org/10.1080/10426509908546178

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 45-48
Reprints available directly from the publisher
Photocopying permitted by license only

Reactivity of a Cationic Phosphenium Complex of Tungsten Containing an Alkyl or a Stannyl Group

HIROSHI NAKAZAWA, MITSURU KISHISHITA and
KATSUHIKO MIYOSHI

Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739–8526, JAPAN

The treatment of $Cp(CO)_2MeW\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}$ with $BF_3{\bullet}OEt_2$, followed by PPh_3, yields $\textit{trans}\text{-}[Cp(CO)_2(PPh_3)W\{\overline{PN(Me)CH_2CH_2N}Me(Me)\}]\ BF_4$, suggesting that a cationic phosphenium complex is first formed and then migratory insertion of the phosphenium ligand into a W-alkyl bond takes place. In the reaction of the stannyl containing complex, $Cp(CO)_2(SnR_3)W\{\overline{PN(Me)CH_2CH_2N}\text{-}Me(OMe)\}$, with TMSOTf, an alkyl migration from Sn to a phosphenium P occurs to give a stannylene complex.

Keywords: phosphenium complex; stannylene complex; migaroty insertion

INTRODUCTION

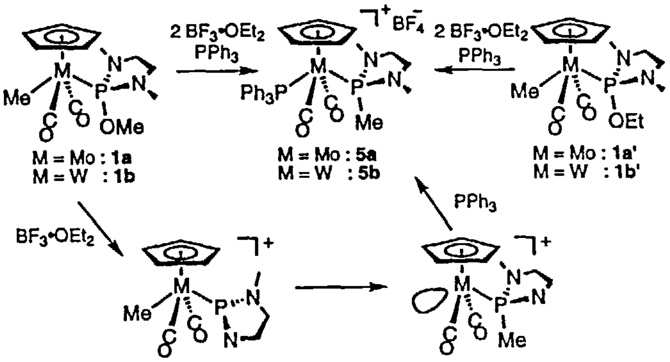
A cationic phosphenium species described as $[PR_2]^+$ has lone pair electrons and a vacant p orbital, so it may serve as a Lewis base and a Lewis acid. The coordination chemistry of these cations has received considerable attention, and many cationic transition-metal phosphenium complexes have been prepared.[1-3] However, the reactivity of these complexes is much less investigated. We have been engaged in the study of the preparation, structures, properties, and reactivities of cationic phosphenium complexes of group 6[4-6] and 8[7,8] transition metals. In this paper we report the results of our recent studies involving cationic phosphenium complexes of Mo and W. In this paper, $\overline{PN(Me)CH_2CH_2N}Me(OR)$ is described an PNN(OR) for simplicity.

PREPARATION OF $Cp(CO)_2(ER_3)M\{PNN(OMe)\}$ (ER_3 = CH_3, $SnPh_3$, $SnMe_3$, Sn^nBu_3; M = Mo, W)

Molybdenum and tungsten complexes containing a methyl group have been prepared from the photoreaction of Cp(CO)$_3$MeM (M = Mo, W) with the diamino-substituted phosphite. The stannyl complexes have been prepared in the reaction of Cp(CO)$_2$(I)M{PNN(OMe)} (the complex can be obtained from Cp(CO)$_3$(I)M and PNN(OMe)) with NaK$_{2.8}$, followed by R$_3$SnCl.

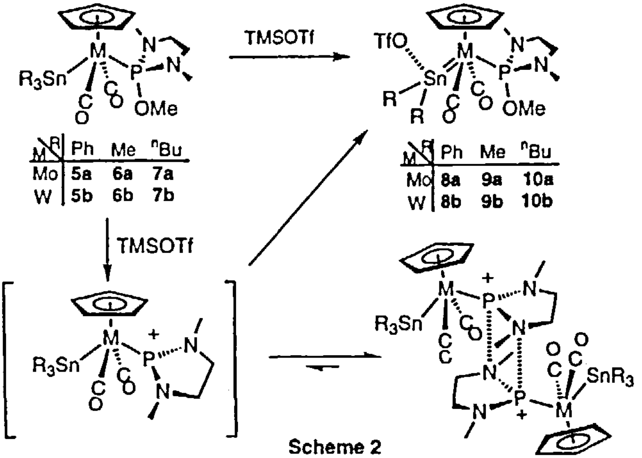
REACTION OF Cp(CO)$_2$(CH$_3$)M{PNN(OR)} with BF$_3$•OEt$_2$ and then PPh$_3$

The reaction of the methyl complex of Mo (**1a**) with BE$_3$•OE$_{t2}$ yields [Cp(CO)$_2$(PPh$_3$)Mo{PNN(Me)}]BF$_4$ (**2a**) (scheme 1). The complex was isolated, characterized spectroscopically, and its structure was confirmed by X-ray crystal analysis. The reaction of **1b** with BF$_3$•OEt$_2$ and then PPh$_3$ yields the corresponding product (**2b**). These reactions imply methyl migration from M to the phosphorus atom. The migration is substantiated by the results of the parallel reactions with BF$_3$•OEt$_2$ and then PPh$_3$ of **1a'** and **1b'** which contain an OEt group in place of an OMe group on the P atom of **1a** and **1b**. The products, **2a** and **2b**, clearly show that the OEt group on the phosphorus atom is eliminated and the Me group on the Mo or W atom migrates to the phosphorus atom.



Scheme 1

The proposed reaction pathway is shown in Scheme 1. In the reaction of **1** with BF$_3$•OEt$_2$, the OR group on the phosphorus atom is abstracted by BF$_3$ to give cationic **3** and [BF$_3$OR]$^-$. The latter BF$_3$OR$^-$ reacts with BF$_3$ to give BF$_2$OR and BF$_4^-$, serving as a counteranion in **2**. Following the formation of **3**, the methyl group bound to M migrates to the phosphenium phosphorus atom to give **4**. Since the cationic intermediate **4** itself is a 16-electron species, it may be stabilized by weak coordination of the solvent or BF$_2$OR, for example. Compound **4** is readily converted into a stable and isolable complex **2** by addition of PPh$_3$.



Scheme 2

REACTION OF $Cp(CO)_2(SnR_3)M\{PNN(OR)\}$ with TMSOTf

$Cp(CO)_2(SnR_3)M\{PNN(OR)\}$ reacts with TMSOTf at room temperature to give *trans*-$[Cp(CO)_2(SnR_2)M\{PNN(Me)\}]OTf$, suggesting that an OMe group is abstracted and one Ph group on the Sn atom migrates to the phosphorus to give a stannylene complex (Scheme 2). The X-ray structures for $[Cp(CO)_2(SnPh_2)W\{PNN(Me)\}]OTf$ (**8b**) and $[Cp(CO)_2(SnMe_2)W\{PNN(Me)\}]OTf$ (**9b**) are shown in Figures 1 and 2, respectively. In both cases, Sn-O(OTf) bond lengths are shorter than the sum of the van der Waals of Sn and O, indicating some interaction between Sn and O. A closer look reveals that **8b**

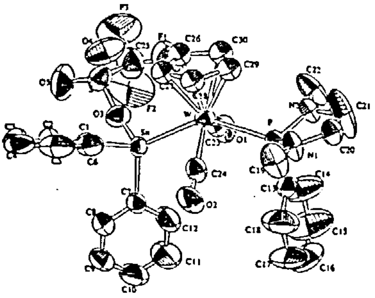


FIGURE 1. ORTEP drawing of **8b** and numbering scheme.

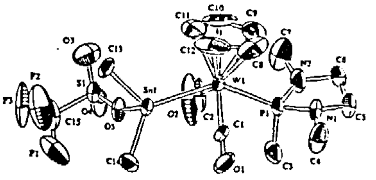


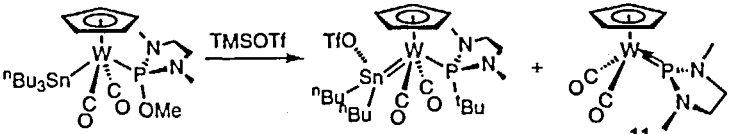
FIGURE 2. ORTEP drawing of **9b** and numbering scheme.

is considered as a stannyl complex (the Sn-O bond length = 2.160 Å, and the sum of angles around Sn = 346.7 °), whereas **9b** is more appropriately considered a stannylene complex (the Sn-O bond length = 2.344 Å, and the sum of angles around Sn = 358.5 °). In the ^{119}Sn NMR spectrum, the products exhibit a doublet at 335.06 ppm for **8b**, a resonance is shifted more than 330 ppm downfield relative to that of the starting complex (-1.98 ppm). Likewise, a doublet at 526.53 ppm attributed to **9b** appears more than 480 ppm downfield shift relative to that of its starting complex (45.04 ppm). Therefore, in solution these products have character of a stannylene complex.

Monitoring the reaction of the stannyl complex with TMSOTf reveals that a dimer of a cationic phosphenium complex is formed in solution, and the monomer is not obserbed in the reaction mixture. We propose mutual interaction where a nitrogen in a phosphenium ligand weakly coordinates to a phosphenium phosphorus in another molecule.

The reaction may proceed as follows (Scheme 2). An OMe group is abstracted by TMSOTf to give a cationic phosphenium complex, which dimerizes through intermolecular N-P interaction. The monomer and dimer are in equilibrium which favors the dimer. An alkyl migration reaction takes place from the monomer to give a stannylene complex.

$Cp(CO)_2(Sn^nBu_3)W\{PNN(OR)\}$ (**10b**) shows the similar reactivity. However, in this case, in addition to **10b**, a 3-electron donor terminal phosphide complex (**11**) is also obtained (Scheme 3). It should be noted here that this complex is apparently formed with elimination of Sn^nBu_3 and OMe. The detail will be reported somewhere.



7b 10b 11

Scheme 3

References

[1]] A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 85, 367 (1985).

[2] M. Samchez, M. R. Mazieres, L. Lamande, and R. Wolf, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, edited by M. Regitz and O. J. Scherer (Thieme, New York, 1990), Chap. D.

[3] D. Gudat, *Coord. Chem. Rev.*, **163**, 71 (1997).

[4] H. Nakazawa, Y. Yamaguchi, T. Mizuta, and K. Miyoshi, *Organometallics*, **14**, 4173 (1995).

[5] Y. Yamaguchi, H. Nakazawa, T. Itoh, and K. Miyoshi, *Bull. Chem. Soc. Jpn.*, **69**, 983 (1996).

[6] Y. Yamaguchi, H. Nakazawa, M. Kishishita, and K. Miyoshi, *Organometallics*, **15**, 4383 (1996).

[7] H. Nakazawa, Y. Yamaguchi, T. Mizuta, S. Ichimura, and K. Miyoshi, *Organometallics*, **14**, 4635 (1995).

[8] H. Nakazawa, Y. Yamaguchi, and K. Miyoshi, *Organometallics*, **15**, 4661 (1996).