

## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpss20>

## Reactivity of Cationic Transition-Metal Phosphenium Complexes

Hiroshi Nakazawa , Yoshitaka Yamaguchi & Katsuhiko Miyoshi

<sup>a</sup> Institute for Molecular Science , Myodaiji, Okazaki 444, Japan

<sup>b</sup> Department of Chemistry, Hiroshima University , Higashi-Hiroshima 739, Japan

Published online: 06 Aug 2008.

To cite this article: Hiroshi Nakazawa , Yoshitaka Yamaguchi & Katsuhiko Miyoshi (1996) Reactivity of Cationic Transition-Metal Phosphenium Complexes, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 109:1-4, 129-132

To link to this article: <http://dx.doi.org/10.1080/10426509608545107>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

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



## REACTIVITY OF CATIONIC TRANSITION-METAL PHOSPHENIUM COMPLEXES

HIROSHI NAKAZAWA, YOSHITAKA YAMAGUCHI, AND KATSUHIKO MIYOSHI

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and  
Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739, Japan

**Abstract** Reactivity of cationic transition-metal phosphonium complexes has been investigated. Reaction of  $\text{mer}-(\text{bpy})(\text{CO})_3\text{M}\{\text{PN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}\}]^+$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) with  $\text{X}^-$  ( $\text{X} = \text{Me}, \text{OEt}$ ) exhibits a nucleophilic attack at the phosphonium phosphorus, whereas that with  $\text{L}$  ( $\text{L} = \text{phosphine}, \text{phosphite}$ ) shows CO/L substitution. Iron phosphonium complexes,  $[\text{Cp}(\text{CO})\text{RFe}\{\text{PN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}\}]^+$  undergoes a migratory insertion of the phosphonium ligand into the Fe-alkyl bond.

**Key Words:** Phosphonium complex, Transition metal, Nucleophilic attack, CO substitution, Migratory insertion.

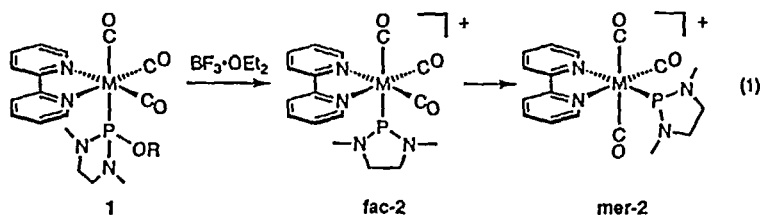
## INTRODUCTION

A phosphonium cation described as  $\text{PR}_2^+$  serves as a unique ligand toward a transition metal. It has both lone pair electrons and a vacant p orbital on the phosphorus atom, thus it can act as a  $\sigma$ -donor and also as a  $\pi$ -acceptor. Although many cationic transition-metal phosphonium complexes and some preparative methods have been reported so far,<sup>1,2</sup> information concerning their reactivity is much more sparse. In this paper, we report our results obtained so far concerning the reactivity of cationic phosphonium complexes.

## PREPARATION OF CATIONIC PHOSPHENIUM COMPLEXES

Before discussing the reactivity of cationic phosphonium complexes, it may be pertinent to show the preparative method of cationic phosphonium complexes we employed.<sup>3,4</sup> Electrically neutral group 6 transition metal complexes with amino-substituted phosphite (1) react with a Lewis acid such as  $\text{BF}_3 \cdot \text{OEt}_2$  to give cationic phosphonium complexes (2) by the abstraction of an OR group as an anion (eq 1). The product has a facial geometry which gradually changes to its meridional form. The isomerization is completed for 1 day for Cr and Mo complexes, whereas the W complex does not

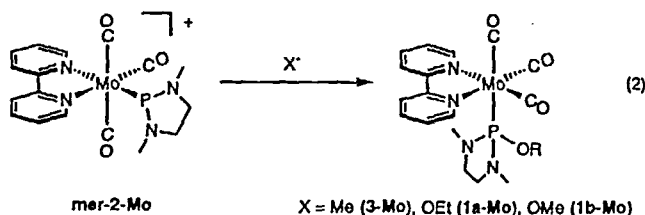
isomerize for several days at room temperature.



These reactions are clean and quantitative and the products are stable in solution at room temperature for several days but sensitive toward air. Several trials to isolate the product in the solid state were unsuccessful. Therefore, these phosphonium complexes were prepared in solution and subjected to further reactions without isolation.

### REACTIVITY WITH $R^-$ , $OR^-$ , AND $HNEt_2$

A cationic phosphonium Mo complex (**mer-2-Mo**) reacted with LiMe and NaOEt to give **3-Mo** and **1a-Mo**, respectively (eq 2), while **1-Mo** did not react with LiMe or NaOEt.<sup>3</sup> Therefore, it was established that **mer-2-Mo** is susceptible to nucleophilic attack at the phosphorus atom.



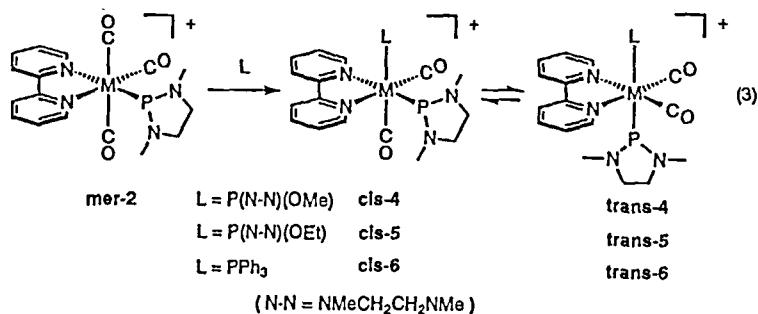
In the reaction with  $HNEt_2$ , **1b-Mo** containing an OMe group was unexpectedly obtained from **mer-2-Mo** and  $HNEt_2$ , both of which have no OMe group. **1b-Mo** may be formed from the reaction of **mer-2-Mo** with  $OMe^-$  which is released by the attack of  $HNEt_2$  on the  $BF_3(OMe)^-$  present.

It is known that cationic carbonyl complexes react with  $OR^-$  to give alkoxy carbonyl complexes.<sup>5</sup> **mer-2-Mo** can be regarded as a cationic carbonyl complex. In this case, nonetheless,  $OR^-$  and  $R^-$  selectively attack the phosphorus atom but not the carbonyl carbon.

### REACTIVITY WITH TRIVALENT PHOSPHORUS COMPOUNDS

The reaction of **mer-2** with a trivalent phosphorus compound (L) in  $CH_2Cl_2$  yielded a  $CQ/L$  substituted product.<sup>6</sup> Two geometrical isomers were detected and it was found that

they were at equilibrium (eq 3).



In the reaction in eq 3, **cis-4** may be formed first. A phosphonium ligand is a strong  $\pi$  acceptor, so three CO ligands in **mer-2**, especially two CO ligands mutually trans are activated by it. Thus, one of the two CO ligands is readily replaced by L to give **cis-4**, which then isomerizes to **trans-4** to reach the equilibrium. It should be noted here that a non-phosphonium complex, **1**, does not undergo CO/L exchange reaction at room temperature.

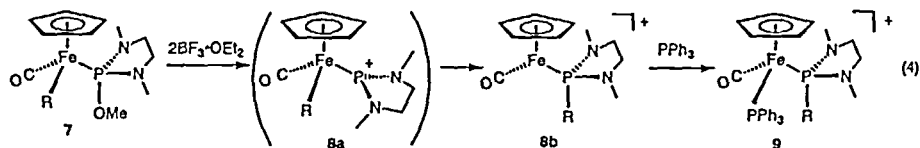
Bpy and L serve as a  $\sigma$ -donor and also as a weak  $\pi$ -acceptor, and the  $\pi$ -acidity is weaker for bpy than for L.<sup>7</sup> Therefore, the cis form where a phosphonium ligand is trans to bpy is electronically favored than the trans form where a phosphonium ligand is trans to phosphite. The  $J_{\text{PW}}$  values of **4-W** indicate that the phosphonium ligand is bonded more strongly to W for the cis form than for the trans form.

A cis/trans isomer ratio was 24/76 for **4-Mo** and 22/78 for **4-W**, whereas 0/100 for **4-Cr**. It is suggested that Cr, having a small radius than Mo or W is too small to accept the two ligands in the cis configuration. The P-P coupling constant for the Cr complex (91.6 Hz) was smaller than that for the Mo (274 Hz) or the W (268.6 Hz) complexes. It is suggested that the phosphite and/or the phosphonium may not approach closely to the small Cr to make a sufficient bond due to the steric repulsion. The ratio of 7/93 for **6-Mo** can be rationalized also by the steric effect. These equilibria are on a critical balance, but basically it can be said that the cis form is electronically and the trans form is sterically favored.

## REACTIVITY OF $\text{Cp}(\text{CO})\text{RFe}\{\text{PN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}(\text{OMe})\}$ WITH $\text{PPh}_3$

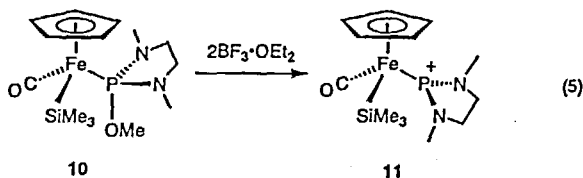
Piano stool iron complexes containing an alkyl group (Me,  $\text{CH}_2\text{Ph}$ ) and diamino-substituted phosphite, **7**, reacted with  $\text{BF}_3 \cdot \text{OEt}_2$  then  $\text{PPh}_3$  to give **9** (eq 4).<sup>8</sup> The reaction may proceed as follow. In the reaction of **7** with  $\text{BF}_3 \cdot \text{OEt}_2$ , an OMe group on a phosphorus is abstracted by  $\text{BF}_3$  as an anion to give a cationic iron phosphonium complex **8a**. Due to its high reactivity, **8a** can not be detected, and undergoes migratory

insertion of a phosphonium ligand into an Fe-alkyl bond (or alkyl migration from iron to phosphonium phosphorus) to give **8b** which is detectable in solution. **8b** is trapped by  $\text{PPh}_3$  to give stable **9**.



Alkyl migration to CO ligand to give an acyl ligand on a transition metal is well known.<sup>9</sup> Complex **8a** has a terminal carbonyl ligand as well as a phosphonium ligand. It is thus notable that an alkyl group migrates exclusively to a phosphonium ligand in the present reaction.

The reaction of a silyl iron complex showed very significant results from the mechanistic aspect. The reaction of **10** with  $\text{BF}_3 \cdot \text{OEt}_2$  in  $\text{CH}_2\text{Cl}_2$  gave a homogeneous solution containing a cationic phosphonium iron complex with a silyl group (**11**) (eq 5).



Treatment of **11** with  $\text{PPh}_3$  caused no reaction. No silyl migration to the phosphonium phosphorus may be due to a stronger Fe-silyl bond than Fe-alkyl bond. However, the detection of the phosphonium complex **11** supports the reaction sequence shown in eq 4.

## REFERENCES

1. A. H. Cowley and R. A. Kemp, *Chem. Rev.*, **85**, 367 (1985).
2. M. Sanchez, 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. D1.
3. H. Nakazawa, M. Ohta, K. Miyoshi and H. Yoneda, *Organometallics*, **8**, 638 (1989).
4. H. Nakazawa, Y. Yamaguchi and K. Miyoshi, *J. Organomet. Chem.*, **465**, 193 (1994).
5. R. J. Angelici, *Acc. Chem. Res.*, **5**, 335 (1972).
6. H. Nakazawa, Y. Yamaguchi, T. Mizuta and K. Miyoshi, submitted for publication.
7. M. H. Chisholm, J. A. Connor, J. C. Huffman, E. M. Koben and C. Overton, *Inorg. Chem.*, **23**, 2298 (1984).
8. H. Nakazawa, Y. Yamaguchi, T. Mizuta, S. Ichimura and K. Miyoshi, submitted for publication.
9. H. M. Colquhoun, D. J. Thompson and M. V. Twigg, in *Carbonylation: Direct Synthesis of Carbonyl Compounds*, (Plenum Press, New York, 1991).