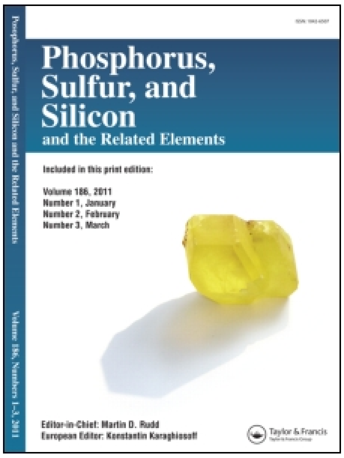

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REACTIVITY OF CATIONIC TRANSITION-METAL PHOSPHENIUM COMPLEXES

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Abstract Reactivity of cationic transition-metal phosphenium complexes has been investigated. Reaction of mer-$[(bpy)(CO)_3M\{PN(Me)CH_2CH_2NMe\}]^+$ (M = Cr, Mo, W) with X^-(X = Me, OEt) exhibits a nucleophilic attack at the phosphenium phosphorus, whereas that with L (L = phosphine, phosphite) shows CO/L substitution. Iron phosphenium complexes, $[Cp(CO)RFe\{PN(Me)CH_2CH_2NMe\}]^+$ undergoes a migratory insertion of the phosphenium ligand into the Fe-alkyl bond.

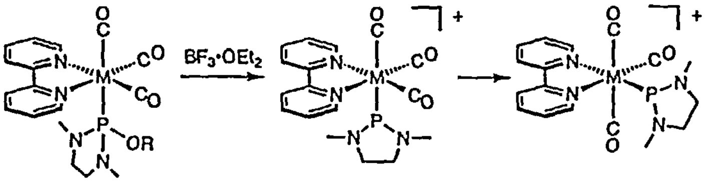
Key Words: Phosphenium complex, Transition metal, Nucleophilic attack, CO substitution, Migratory insertion.

INTRODUCTION

A phosphenium cation described as 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 σ-donor and also as a π-acceptor. Although many cationic transition-metal phosphenium complexes and some preparative methods have been reported so far, [1,2] information concerning their reactivity is much more sparse. In this paper, we report our results obtained so far concerning the reactivity of cationic phosphenium complexes.

PREPARATION OF CATIONIC PHOSPHENIUM COMPLEXES

Before discussing the reactivity of cationic phosphenium complexes, it may be pertinent to show the preparative method of cationic phosphenium complexes we employed.[3,4] Electrically neutral group 6 transition metal complexes with amino-substituted phosphite (**1**) react with a Lewis acid such as $BF_3 \cdot OEt_2$ to give cationic phosphenium 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.



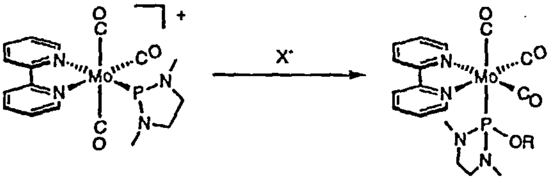
1 fac-2 mer-2

(1)

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 phosphenium complexes were prepared in solution and subjected to further reactions without isolation.

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

A cationic phosphenium 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.[3] Therefore, it was established that **mer-2-Mo** is susceptible to nucleophilic attack at the phosphorus atom.



mer-2-Mo X = Me (3-Mo), OEt (1a-Mo), OMe (1b-Mo)

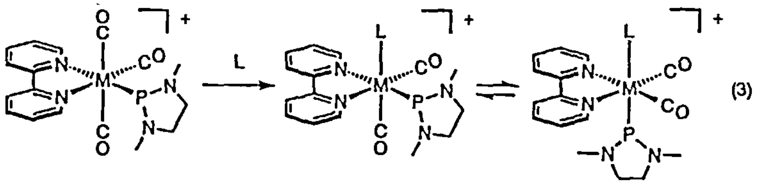
(2)

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.[5] **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 CO/L substituted product.[6] Two geometrical isomers were detected and it was found that they were at equilibrium (eq 3).



(3)

mer-2

L = P(N-N)(OMe) cis-4 trans-4

L = P(N-N)(OEt) cis-5 trans-5

L = PPh_3 cis-6 trans-6

(N-N = $NMeCH_2CH_2NMe$)

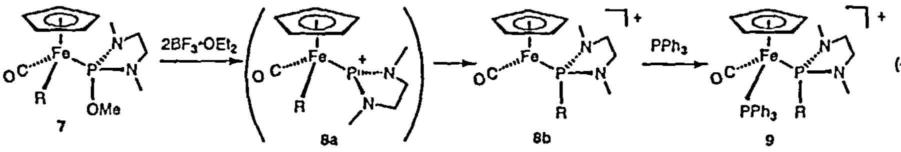
In the reaction in eq 3, **cis-4** may be formed first. A phosphenium ligand is a strong π acceptor, so three CO ligands in **mer-2**, especially two CO ligands mutually trans are activated by it. Thus, one of the two CO ligands is readily replaced by L to give **cis-4**, which then isomerizes to **trans-4**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

Bpy and L serve as a σ-donor and also as a weak π-acceptor, and the π-acidity is weaker for bpy than for L.[7] Therefore, the cis form where a phosphenium ligand is trans to bpy is electronically favored than the trans form where a phosphenium ligand is trans to phosphite. The J_{PW} values of **4-W** indicate that the phosphenium 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 lignads 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 phosphenium 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 equilibriums are on a critical balance, but basically it can be said that the cis form is electronically and the trans form is sterically favored.

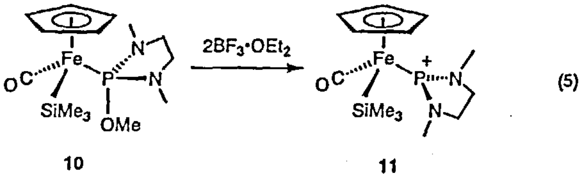
REACTIVITY OF Cp(CO)RFe{PN(Me)CH_2CH_2NMe(OMe)} WITH PPh_3

Piano stool iron complexes containing an alkyl group (Me, CH_2Ph) and diamino-substituted phosphite, **7**, reacted with $BF_3{\cdot}OEt_2$ then PPh_3 to give **9** (eq 4).[8] The reaction may proceed as follow. In the reaction of **7** with $BF_3{\cdot}OEt_2$, an OMe group on a phosphorus is abstracted by BF_3 as an anion to give a cationic iron phosphenium complex **8a**. Due to its high reactivity, **8a** can not be detected, and undergoes migratory insertion of a phosphenium ligand into an Fe-alkyl bond (or alkyl migration form iron to phosphenium phosphorus) to give **8b** which is detectable in solution. **8b** is trapped by PPh_3 to give stable **9**.



Alkyl migration to CO ligand to give an acyl ligand on a transition metal is well known.[9] Complex **8a** has a terminal carbonyl ligand as well as a phosphenium ligand. It is thus notable that an alkyl group migrates exclusively to a phosphenium 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 $BF_3 \cdot OEt_2$ in CH_2Cl_2 gave a homogeneous solution containing a cationic phosphenium iron complex with a silyl group (**11**) (eq 5).



Treatment of **11** with PPh_3 caused no reaction. No silyl migration to the phosphenium phosphorus may be due to a stronger Fe-silyl bond than Fe-alkyl bond. However, the detection of the phosphenium complex **11** supports the reaction sequence shown in eq 4.

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