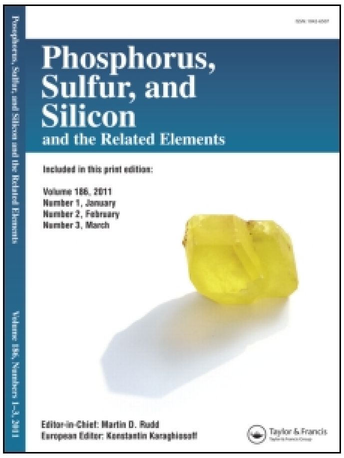

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# Addition of AlkylHalide toward a Tungsten-Phosphorus Double Bond

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# ADDITION OF ALKYLHALIDE TOWARD A TUNGSTEN–PHOSPHORUS DOUBLE BOND

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*The terminal phosphide complex of tungsten* $Cp(CO)_3W\{PN(Me)CH_2CH_2PNMe\}$ *(**3**) prepared from* $Cp(Sn^nBu_3)(CO)_2W\{PN(Me)CH_2CH_2NMe(OMe)\}$, $BF_3\cdot OEt_2$, *and* $NaBPh_4$ *in situ reacts with* $PhCH_2Cl$ *to give cis-*$Cp(CO_2)ClW\{PN(Me)CH_2CH_2NMe(CH_2Ph)\}$ *(**cis-4**). During the reaction, C—Cl bond addition takes place toward a tungsten–phosphorus double bond. In contrast, isolated **3** does not react with* $PhCH_2Cl$*. Isolated **3**, however, reacts with* $PhCH_2Cl$ *in the presence of* $BPh_3$ *and* $BF_3$ *to give **trans-4** and **cis-4**, respectively.*

*Keywords:* Addition reaction; double bond; terminal phosphide complex

A transition-metal complex bearing a three-electron donor terminal phosphide ligand has attracted considerable attention because the complex possesses a double bond between a transition metal and a phosphorus atom. Recently, we found a new method for preparation of a terminal phosphide complex. A tungsten complex having diamino-substituted phosphite and a stannyl ligand (**1**) reacts with TMSOTf to give a phosphenium complex (**2**) and a phosphide complex (**3**, 27%), (Figure 1).[1] In contrast, when **1** is treated with $BF_3\cdot OEt_2$ in the presence of $NaBPh_4$, the product is only **3** (100% yield based on the $^{31}$P-NMR spectrum, 83% isolation yield). Here we report the reaction of the phosphide complex **3** with alkylhalide.

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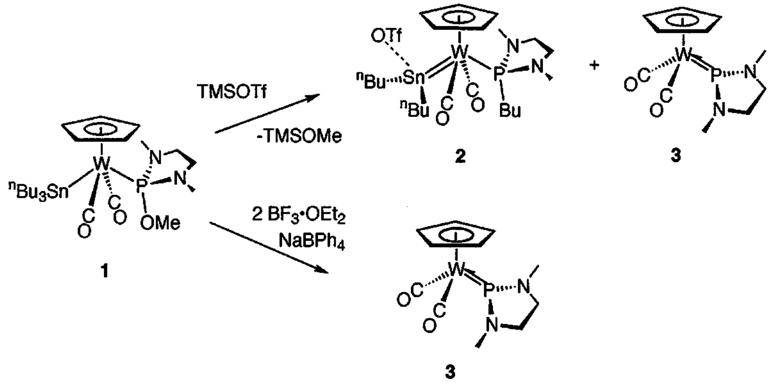

FIGURE 1

## REACTION OF THE PHOSPHIDE COMPLEX WITH BENZYLCHLORIDE

Since the reaction of **1** with BF$_3$•OEt$_2$ in the presence of NaBPh$_4$ proceeds cleanly in CH$_2$Cl$_2$ at room temperature to give the phosphide complex **3**, we added benzylchloride to **3** prepared in situ in order to examine the reaction of **3** with PhCH$_2$Cl (Figure 2). The reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residue was purified with an alumina column to give an orange powder of **cis-4** (Figure 2). In the reaction, the C—Cl bond in PhCH$_2$Cl is selectively added to the W—P double bond of **3** with P—C and W—Cl bond formation. It was found that **cis-4** is a kinetic

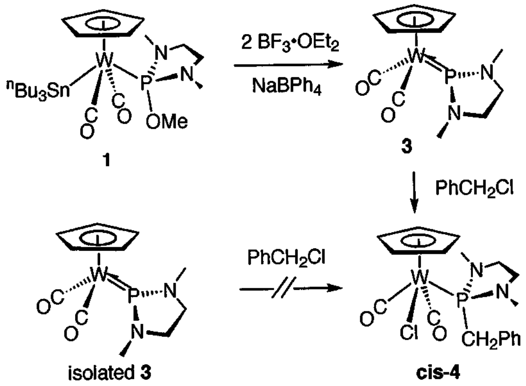

FIGURE 2

product, because **cis-4** gradually isomerizes to **trans-4** in solution and finally the cis and trans isomers reach the equilibrium with 2:1 molar ratio.

In contrast, interestingly, the isolated **3** does not react with $PhCH_2Cl$. These unexpected results show that something present in a reaction mixture of **1**, $BF_3{\cdot}OEt_2$, and $NaBPh_4$ may play a crucial role to drive the reaction of **3** with $PhCH_2Cl$ to give **cis-4**.

## REACTION OF ISOLATED 3 WITH PhCH$_2$Cl IN THE PRESENCE OF BPh$_3$

After several attempts to identify the species that promotes the reaction of **3** with $PhCH_2Cl$, we finally found that some borane compounds serve well.

As mentioned earlier, isolated **3** does not react with $PhCH_2Cl$ in $CH_2Cl_2$ at room temperature. However, if $BPh_3$ is added, a reaction takes place and the product is chloro diamino-substituted phosphine complex with a trans geometry (**trans-4**) (Figure 3). This reaction shows that $BPh_3$ promotes the $PhCH_2Cl$ addition to the W—P double bond, but the kinetic product is not **cis-4** but **trans-4**.

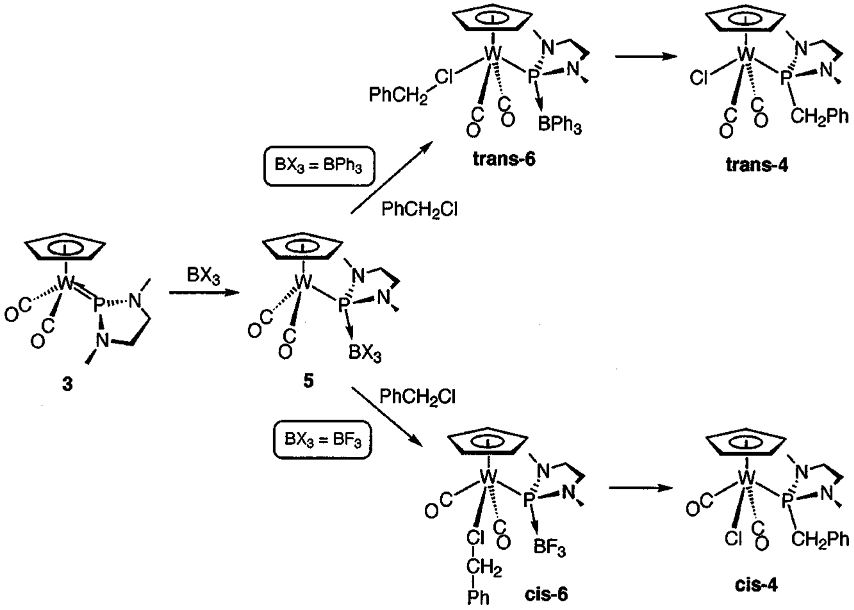

FIGURE 3

## REACTION OF ISOLATED 3 WITH $PhCH_2Cl$ IN THE PRESENCE OF $BF_3$

It was found that $BF_3$ also promotes the conversion of **3** into the addition product in the reaction of $PhCH_2Cl$. In this case, the kinetic product has a cis geometry.

We propose the reaction sequences as follows (see Figure 3). Since $BX_3$ is an electron deficient compound, $BX_3$ may make a dative bond with the lone pair electrons on the phosphorus in **3**. The complex **5** thus formed is electron deficient at the tungsten (16e species), because two electrons from the phosphorus are donated to the added $BX_3$. Then $PhCh_2Cl$ can coordinate to the W atom of **5** through the lone-pair electrons on the Cl atom to give **6**. If $BX_3$ is relatively bulky $BPh_3$, the product may have a trans geometry (**trans-6**), and if $BX_3$ is less bulky $BF_3$, the product may have a cis geometry (**cis-6**). The following release of $BX_3$ from the phosphorus leads to C—Cl bond activation to give **4**, keeping the geometry around the W.

## REFERENCE

[1] H. Nakazawa, M. Kishishita, T. Ishiyama, T. Mizuta, and K. Miyoshi, *J. Organomet. Chem.*, **617–618,** 453 (2000).