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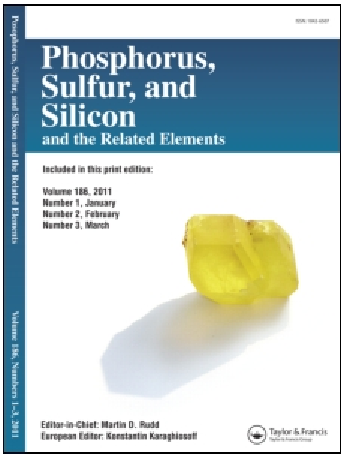

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Reactivity of Phosphaalkenes toward Carbene Complexes

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REACTIVITY OF PHOSPHAALKENES TOWARD CARBENE COMPLEXES

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Reaction of phosphaalkenes $RP{=}C(NMe_2)_2$ ($R = $ t-Bu, Me_3Si), featuring an inverse distribution of electron density about the P—C double bond, with Fischer carbene complexes $[(CO)_5M{=}C(OEt)Ar]$ ($Ar{=}Ph$, $2\text{-}MeC_6H_4$, $2\text{-}MeOC_6H_4$, $M = Cr, W$) afforded a mixture of complexes $[(CO)_5M\{P(R){=}C(NMe_2)_2\}]$ and $[(CO)_5M\{P(R){=}C(OEt)Ar\}]$. The treatment of phosphaalkene $HP{=}C(NMe_2)_2$ with compound $[(CO)_5W{=}C(OEt)(2\text{-}MeOC_6H_4)]$ gives rise to the formation of an (E/Z)-mixture of $[(CO)_5W\{P(CH(NMe_2)_2){=}C(OEt)(2\text{-}MeOC_6H_4)\}]$.

Keywords: Carbene ligand; chromium; insertion; phosphaalkenes; tungsten

The vast majority of phosphaalkenes feature an electron distribution $P^{\delta+}C^{\delta-}$ at the P—C double bond, as would be anticipated from the different electonegativities of carbon (2.5) and phosphorus (2.1).[1] Recently we have become interested in phosphaalkenes with an inverse polarity of the P—C double bond, which means that negative charge is accumulated at the phosphorus atom and a deficiency of charge resides on the carbon atom. This situation is given when one or two amino substituents are linked to the carbon atom of the P=C unit.

Formula **B** (Figure 1) underlines the nucleophilic character of the phosphorus atom in such species. Here we give an account on the reactivity of phosphaalkenes of the type $RP{=}C(NMe_2)_2$ ($R = Cp^*(CO)_2Fe$, H, *t*Bu, Me_3Si) toward Fischer carbene complexes.

When ferriophosphaalkene **1** was exposed to 2 molar equivalents of the Cr- and W-methyl carbene complexes, the formation of novel ferriophosphaalkene-pentacarbonyl metal complexes **2** and β-amino-alkenyl carbene complexes **3** was observed (Figure 2). The combination of the corresponding phenyl carbene complexes

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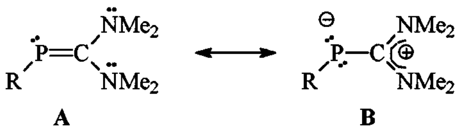


FIGURE 1

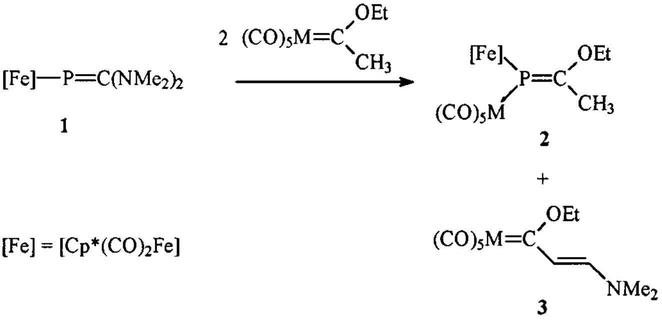
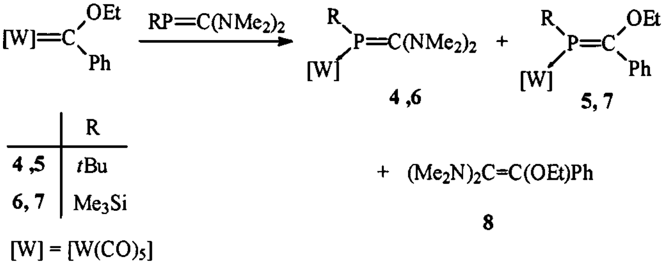


FIGURE 2



	R
4 ,5	*t*Bu
6, 7	Me3Si

[W] = [W(CO)5]

FIGURE 3

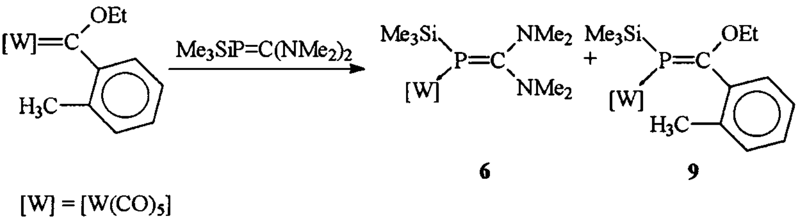
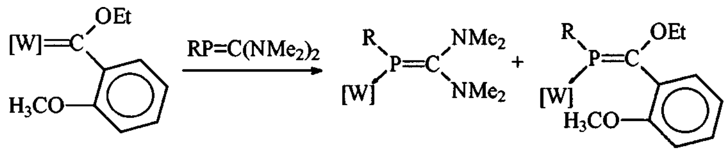


FIGURE 4



4, 6 **10, 11**

	R	yield [%]
10	*t*Bu	39
11	Me_3Si	21

+ $(Me_2N)_2C{=}C(OEt)(2\text{-}MeOC_6H_4)$

12

[W] = $[W(CO)_5]$

FIGURE 5

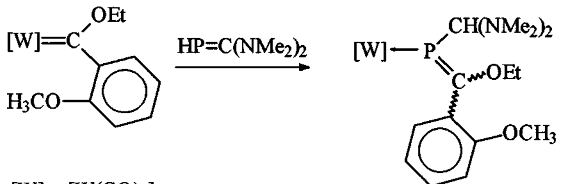
with **1** in *n*-pentane did not give tractable metathesis products. Instead, the dimeric complex $[Cp^*(CO)_2Fe]_2$ (70%) and the adduct $(CO)_5Cr[P\{[Fe]{=}C(NMe_2)_2\}]$ (10%) were isolated. Obviously, this reaction was dominated by the cleavage of the Fe—P bond of **1**.[2]

Treatment of the tungsten phenyl carbene complex with the metal-free phosphaalkenes $RP{=}C(NMe_2)_2$ ($R = t$-Bu, Me_3Si) gave a mixture of the metathesis products **5** and **7** with the complexes **4** and **6** and olefin **8** (Figure 3).[3] Unfortunately, **5** and **7** could not be isolated without decomposition.

An *o*-tolyl carbene tungsten complex did not react with *t*-$BuP{=}C(NMe_2)_2$; whereas with $Me_3SiP{=}C(NMe_2)_2$ complexes **6** and **9** could be isolated as yellow crystals (Figure 4).

The related *o*-anisyl carbene tungsten complex and the phosphaalkenes $RP{=}C(NMe_2)_2$ ($R = t$Bu, Me_3Si) underwent reaction to yield mixtures of the adducts **4** and **6** in addition to the metathesis products **10** and **11** and alkene **12** (Figure 5).

Treatment of $HP{=}C(NMe_2)_2$ with $(CO)_5W{=}C(OEt)Ar$ ($Ar = Ph$, 2-MeC_6H_4) has led to decomposition. With the *o*-anisyl carbene complex, however, the formation of the novel phosphalkene complex **13** as a (*E*/*Z*) mixture (1:2) (80% yield) was observed (Figure 6).



[W] = $[W(CO)_5]$

13

FIGURE 6

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