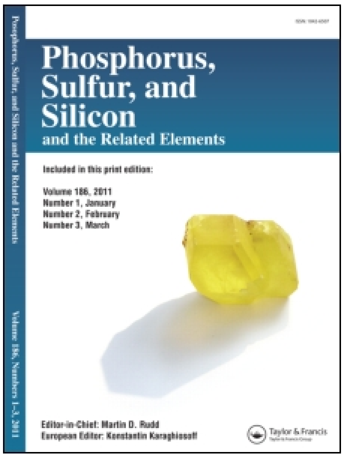

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On the Reactivity of Disilylphosphido Complexes of Transition Metals Towards Acid Chlorides

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ON THE REACTIVITY OF DISILYLPHOSPHIDO COMPLEXES OF TRANSITION METALS TOWARDS ACID CHLORIDES

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Abstract The first phosphaalkenyl complex $Cp(CO)_2Fe\text{-}P{=}C(OSiMe_3)(t\text{-}Bu)$ was generated from $Cp(CO)_2FeP(SiMe_3)_2$ and t-Bu(CO)Cl. In order to test the validity of this synthetic approach, we varied the ring ligand (Cp, C_5Me_5), the metal (Fe, Ru, Os), the main group element (P, As), and the carbonyl chlorides. The diphosphenyl complexes $(C_5Me_5)(CO)_2M\text{-}P{=}P\text{-}[2,4,6\text{-}t\text{-}Bu_3C_6H_2]$ were obtained from $(C_5Me_5)(CO)_2M\text{-}P(SiMe_3)_2$ and the corresponding phosphonous chloride. These metallated diphosphenes are easily converted to diphospho-ureas by treatment with $Fe_2(CO)_9$.

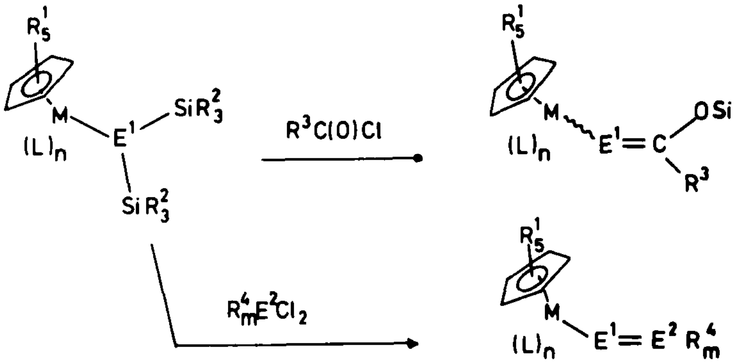
Recently we published the synthesis and X-ray structure analysis of the first phosphaalkenyl complex **1** following a procedure that had been worked out by Becker et al for the preparation of phosphaalkenes.

$$(C_5H_5)(CO)_2FeP(SiMe_3)_2 \xrightarrow[-Me_3SiCl]{+t\text{-}BuC(O)Cl} \underset{\mathbf{1}}{Z\text{-}(C_5H_5)(CO)_2FeP{=}C(OSiMe_3)(t\text{-}Bu)}$$

A similar reaction took place with benzoyl chloride and mesitoyl chloride.

In the following we were interested to test the generality of this synthetic approach to transition metal-substituted phosphaalkenes.

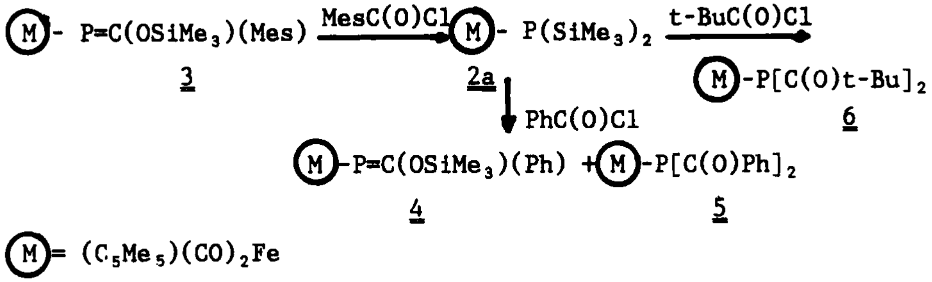
The variations which are reasonable in this system are depicted in the scheme.



Variations are possible a) at the ring, b) at the metal M and the ligands L, and c) at the element E^1 of the complex I.

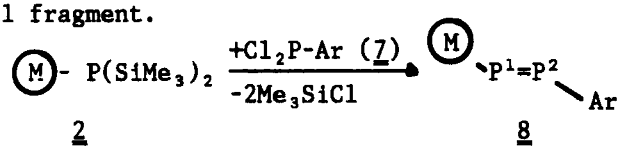
The electrophile also allows variations. In the carbon acid chlorides the organic rest R^2 can be changed. Instead of an organic acid chloride the employment of inorganic acid chlorides of the general Type $R^3{}_mE^2Cl_2$ may lead to novel complexes with unsupported P=P, P=As, P=Ge, P=Sn-double bonds.

First we replaced the C_5H_5-ring at iron by the more bulky and more electron releasing C_5Me_5-ligand. The reaction of the corresponding disilylphosphido complex 2 with an equimolar amount of mesitoyl chloride leads to the expected phosphaalkenyl complex 3. With benzoyl chloride, however a mixture of the phosphaalkenyl complex 4 and the diacylphosphido complex 5 was obtained. The diacylphosphido complex 6 was the sole product of the transformation of 2 with pivaloyl chloride.



The exchange of Fe by the higher homologues Ru and Os leads to a similar reaction pattern. The tendency to form diacylphosphido products instead of phosphaalkenyl complexes however is more pronounced with the heavier and more basic homologues.

In the next step we switched from carbon acid chlorides to organophosphonous chlorides $RPCl_2$. The reaction of the disilylphosphido complexes 2a (M = Fe) and 2b (M = Ru) with 7 cleanly yielded the first diphosphenyl complexes 8a, b in which the unsupported double bond of a diphosphene is linked to a transition metal fragment.

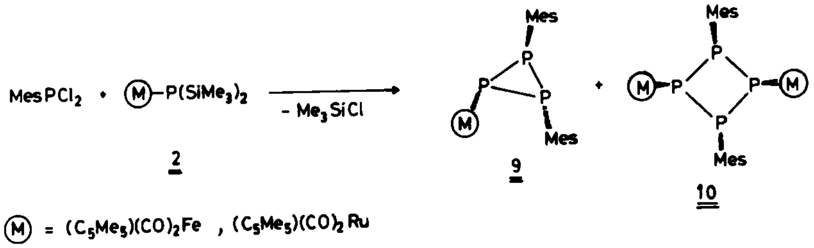


	Ⓜ	δ^1	δ^2	$^1J_{P^1P^2}$/Hz
8a	$(C_5Me_5)(CO)_2Fe$	720.0	552.9	597.4
8b	$(C_5Me_5)(CO)_2Ru$	667.8	551.4	595.8

Ar = 2,4,6-t-$Bu_3C_6H_2$

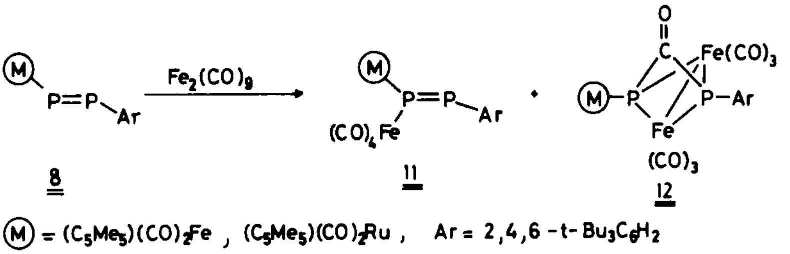
The low-field shift of the metal-bonded phosphorus atoms in the ^{31}P-NMR spectra is remarkable. The X-ray structure analysis of the iron derivative 8a confirmed the identity of the complex unambigiously ($d(P^1{=}P^2) = 201.9(15)$ pm).

The steric requirements of substituents at the phosphorus-phosphorus double bonds are crucial for the formation of the diphosphenyl complexes. Thus with mesityl phosphorus dichloride the first transition metal-substituted cyclotriphosphanes 9 and cyclotetraphosphanes 10 were obtained.



With $(C_5H_5)(CO)_2FeP(SiMe_3)_2$ no characterizable products were generated but the employment of the more bulky complex $(C_5H_5)(CO)(PPh_3)FeP(SiMe_3)_2$ allowed the preparation of diphosphenyl complexes.

The diphosphenyl complexes 8a, b exhibited a very interesting reactivity towards $Fe_2(CO)_9$.



It is the first example of a transition metal-mediated carbonylation of a diphosphene to give a ligated diphospho-urea system. The configuration of products 11 and 12 were established by X-ray diffraction.

Summary

Our investigations demonstrate that the reaction of disilylphosphido complexes with organic and inorganic acid chlorides provides a powerful tool for the synthesis of novel complexes with phosphaalkenyl, diphosphenyl, cyclotriphosphido, and diacylphosphido ligands.