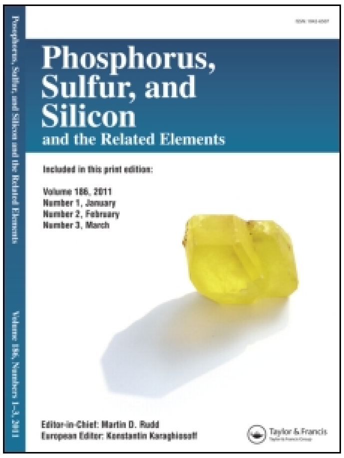

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Diphosphiranes: New Precursors of σ - or π - Diphosphaallyl Complexes

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DIPHOSPHIRANES :
NEW PRECURSORS OF σ - or π - DIPHOSPHAALLYL COMPLEXES.

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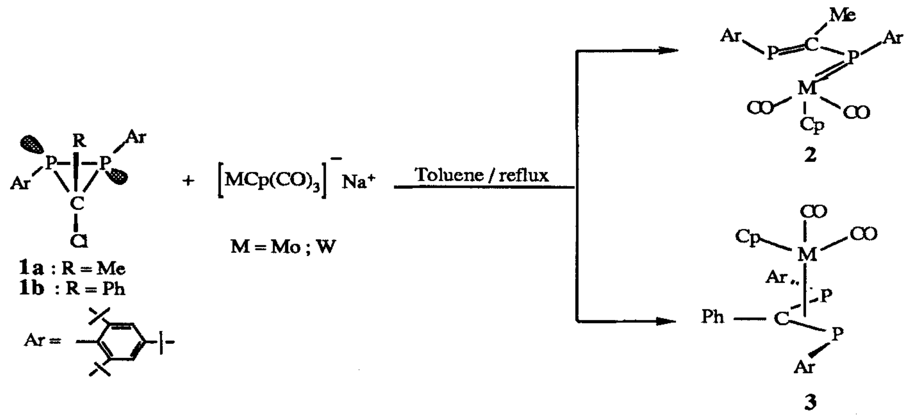
Abstract The metalation reactions of the functionalized diphosphiranes **1a-b** with the anionic metal transition complexes (M = Mo, W, Co) afford the σ- or π- diphosphaallyl complexes (**2** or **3**, respectively) as function of the intracyclic carbon atom substituents. The thermal lability of these complexes is detected by variable-temperature NMR spectroscopy.

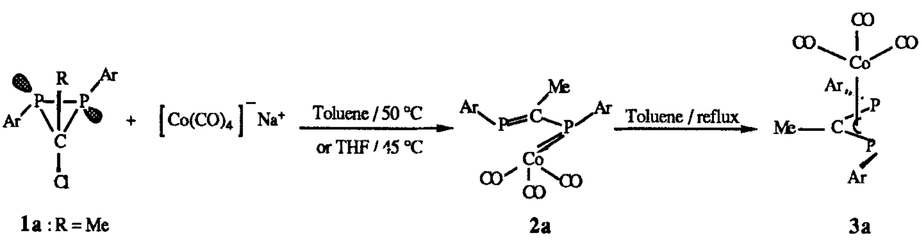
The availability of allylic complexes of transition metals from cyclopropanes has allowed a large development of these systems in catalysis.[1] The presence of phosphorus atom (s) in the 3-membered strained rings modifies the complexation reactions since allylic or cyclic (η^1 and η^3) complexes can be obtained.[2] In the diphosphirane series, the cyclic complexes was first prepared by Huttner[3] *via* the condensation of diphosphene complex with carbenoids. A related chemistry was reported by Weber[4] for the synthesis of transition-metal substituted diphosphaspiropentanes. A more recent work of Stelzer[5] involves the reaction of methylene bis-[dichlorophosphines] with $Fe_2(CO)_9$. It must be pointed out here that all the available data concerning the formation of η^1 cyclic complexes occurs by cycloaddition or metalation of the starting products and not by direct metalation of diphosphirane derivatives.

Here, starting from the diphosphiranes **1a-d** previously described,[6] we report the first examples of their complexation reaction with transition metal complexes.

The reaction of the mono-halogenodiphosphiranes **1a-b** with $[MCp(CO)_3]^- Na^+$ (M = Mo, W), afforded both types of allylic complexes (σ and π) as function of the nature of the intracyclic carbon atoms. So, with R = Me, **1a**, the reaction occurs in refluxing toluene affording the η^1-diphosphaallyl molybdenum or tungsten complexes **2**. On the other hand, **1b** (R = Ph) reacts with the same transition metal complexes in the same conditions to give the η^3-diphosphaallyl complexes **3**. By a completely different approach, Karsch and coll.[7] had already realized the synthesis of analogous η^1-complexes **2** from the unsubstituted 1,3-diphosphapropenes, and they not obtained any η^3-complexes **3** (Mo, W). However, Appel prepared such complexes by the same method with cobalt, nickel and iron complexes.[8]

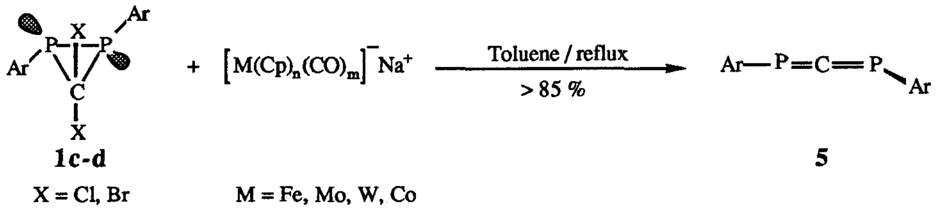


With the cobalt complexes, we observe the same selectivity that for molybdenum and tungsten complexes: the η^3-diphosphaallyl complex **3b** is obtained from **1b**, and the η^1-diphosphaallyl complex **2a** from **1a**. However, upon heating, the phosphido cobalt complex **2a** is transformed into the π-allylic complex **3a**. No reversible reaction was observed whereas such equilibrium between (η^1-phosphaallyl)- and (η^3-phosphaallyl)-tungsten complexes has already described by Mathey and coll..[9]



Nevertheless, the complexation reactions do not take place in all cases. So, treatment of diphosphiranes **1a-b** with $[FeCp(CO)_2]^-$ Na^+ in refluxing toluene solution yields the reduced 1,3-diphosphapropenes **4**. This observation suggests that under these reaction conditions, the [cyclopentadiene iron dicarbonyl] anion decomposes to reducing agent π-$CpFe(CO)_2H$.

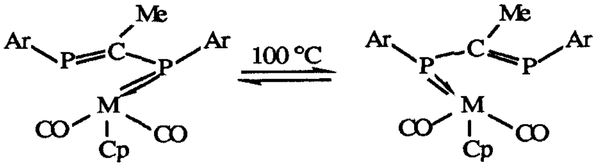
On the other hand, the gem-dihalogenodiphosphiranes **1c-d** react with all the anionic complexes of transition metal and leads quantitatively to 1,3-diphosphaallene **5**, whatever the nature of metal (M = Fe, Mo, W, Co). No diphosphaallyl or cyclic complexes intermediate are detected.



Structure and Thermal Lability of σ- and π- Diphosphaallyl Complexes

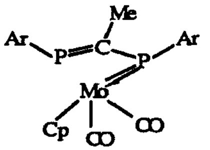
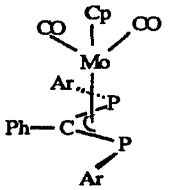
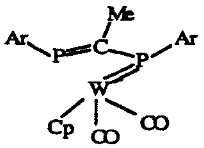
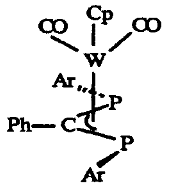
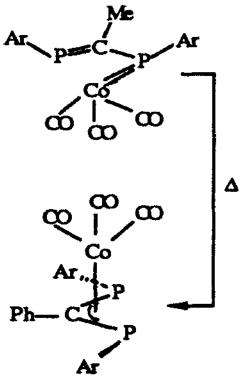
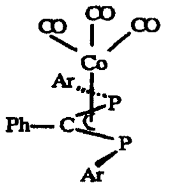
The ^{31}P NMR signals of the σ-complexes are a low field shifted AB system ($274 < \delta < 350$) while the π-complexes resonance is high field shifted ($5 < \delta < 65$) and reflects the equivalence of the both phosphorus atoms (Table I). As expected, for compounds **2** (M = W), the very large $^1J_{PW}$ coupling constant of 700 Hz suggests an sp^2 hybridization of the phosphorus atom. On the contrary, the fully delocalized tungsten complex **3** has a low J_{PW} coupling constant of 137 Hz.

The ^{31}P NMR data of complexes **2** and **3** exhibit an important reversible temperature dependence. Upon heating, all the AB spectra of **2** in toluene coalesce and give a singlet. These observations are the consequence of the fast exchange between the metal (in the endo position) and the two phosphorus atoms.



The singlet signal of the π-complexes **3** obtained at room temperature, splitted to an AB system at low temperature (-100 °C). These anisotropy of the two phosphorus can be explained by the distorsion of the $P\text{-}C_{ipso}$ bond, out the PCP plane. The recent X-ray structure of diphosphaallyl lithium compound corroborates this hypothesis.[10]

Table I - ^{31}P NMR parameters of σ- and π-diphosphaallyl complexes **2** and **3**

σ- diphosphaallyl complex **2**	$\delta\,^{31}P$	π- diphosphaallyl complex **3**	$\delta\,^{31}P$
	331 (P_A) 327 (P_B) J_{PP} = 110 Hz		65
	328 (P_A) 274 (P_B) J_{PP} = 112 Hz J_{PW} = 700 Hz		5.1 J_{PW} = 137 Hz
	350 (broad) 61		64

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