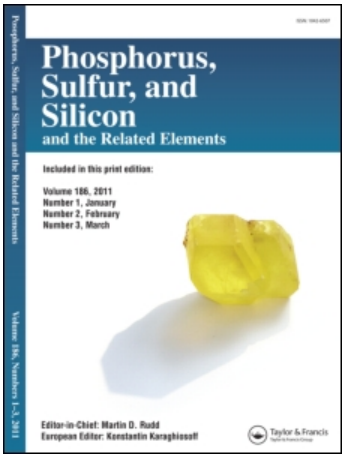

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Multifunctional Neutral Phosphenium Ion Complexes

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MULTIFUNCTIONAL NEUTRAL PHOSPHENIUM ION COMPLEXES

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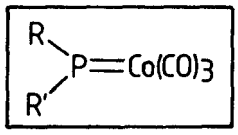
Abstract

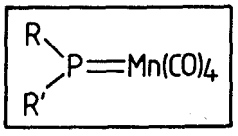
The synthesis, structural features and reactivity of the neutral phosphenium ion complexes (R)(R′)P=ML_n (ML_n = $Co(CO)_3$, $Mn(CO)_4$, $MoCp(CO)_2$; R= 2,4,6-$^tBu_3C_6H_2O$; R′ = C≡CPh, CH=CHPh, $CH_2C{\equiv}CH$, $CH{=}C{=}CH_2$) will be discussed.

Synthesis

Complexes of the type (R)(R′)P=ML_n (ML_n, R, R′ = see above), 1 - 3, can be prepared either via reductive dehalogenation of (R)(R′)PCl with $Co_2(CO)_8$[1] or via NaCl metathesis reaction of (R)(R′)PCl with $NaML_{n+1}$ (ML_{n+1} = $Co(CO)_4$[1], $Mn(CO)_5$[2], $MoCp(CO)_3$[3]). Decarbonylation of (R)(R′)P-ML_{n+1} affords then 1 - 3. 1 and 2 are the first examples of this type of compounds with a phosphorus-cobalt (1) or a phosphorus-manganese (2) π-bond.



1



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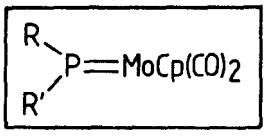


3

Structure, Spectra

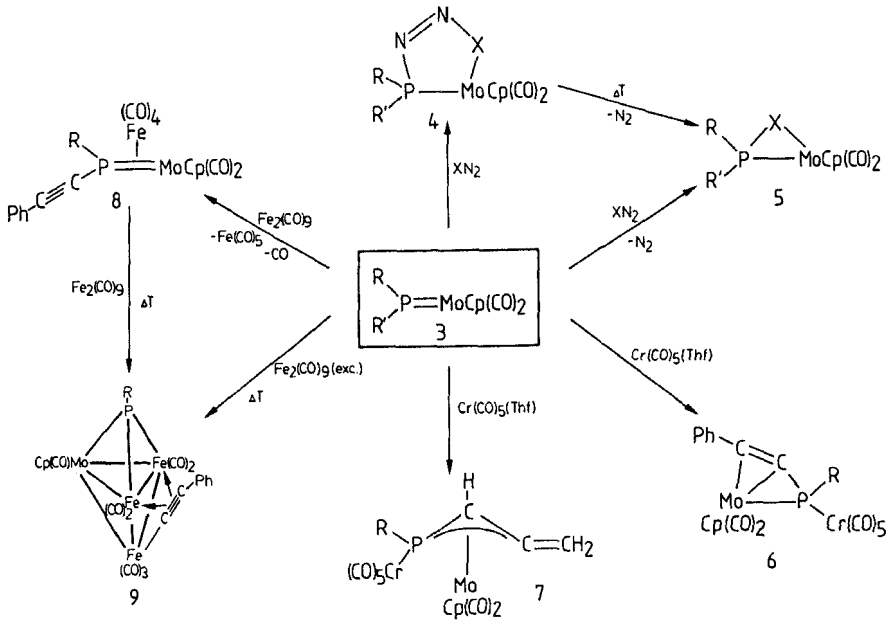
The trigonal planar coordination with short P—M bond lengths is common to all (R)(R′)P=ML_n compounds 1 - 3[1-8]. Such bond shortening can be taken to imply P=M multiple bonding in 1 - 3.

1 - 3 show bright colours due to their P=M multiple bond. The observed down field shift in the ^{31}P-NMR spectra of 1 - 3 is typical for complexes with a sp^2-hybridised phosphorus atom[4].

Reactivity

Some typical reactions of **1** - **3**, with CH_2N_2, PhN_3 and organometallic complex fragments, isolobal to carbene, are shown in scheme 1[5].

1,3-dipolar cycloaddition of CH_2N_2 or PhN_3 with the formal PMo double bond yields the five-membered cycles of **4**. On warming up **4** eliminates N_2 yielding **5** (scheme 1).

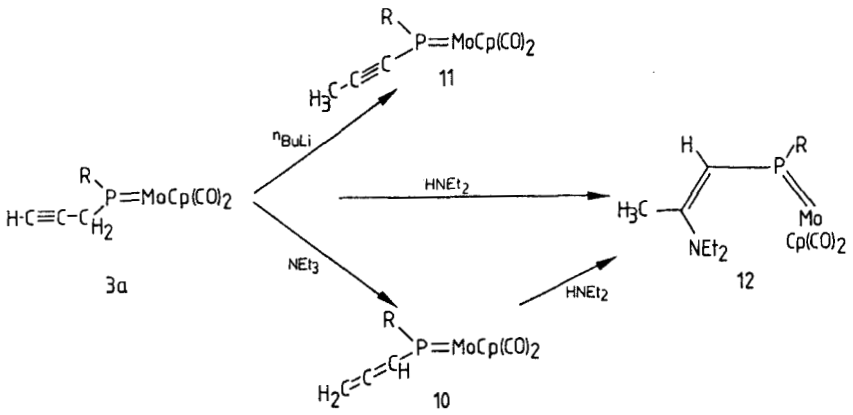


Scheme 1: Reaction of **3** with XN_2 (X = CH_2, NPh), $Fe_2(CO)_9$ and $(CO)_5Cr(Thf)$.

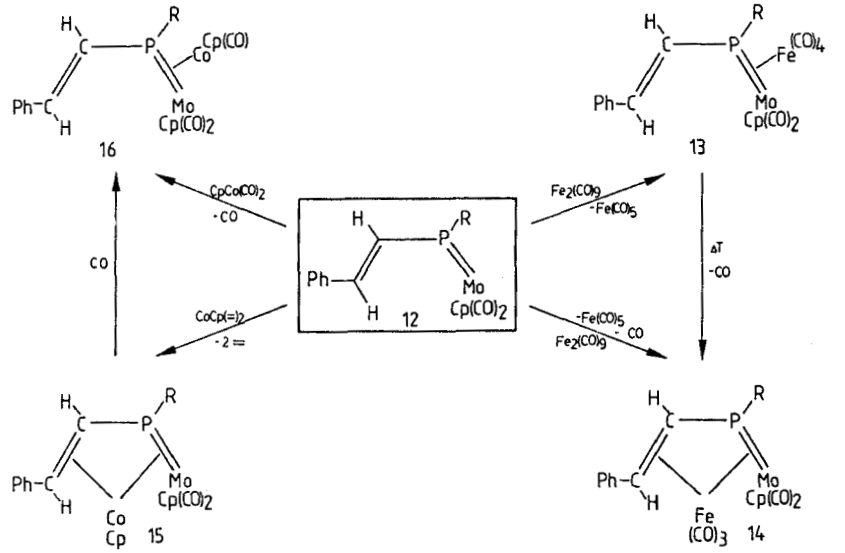
An easy access to 1-phosphaallyl complexes (**7**) is given by the propargyl-allenyl isomerization in (R)($HC{\equiv}CCH_2$) P=$MoCp(CO)_2$, **3a**, induced by $Cr(CO)_5(Thf)$ in Thf, whereas the reaction of the phenylethynyl substituted derivative **3b** yields **6** (scheme 1)[5]. However, with $Fe_2(CO)_9$ the addition of $Fe(CO)_4$ to the formal PMo double bond is observed (**8**; scheme 1)[5]. If an excess of $Fe_2(CO)_9$ is used, the phosphorus-alkynyl-carbon-σ-bond in **3b** is broken and cluster **9** is formed (scheme 1)[5].

Another possibility for initiating the 2-propynyl isomerization in **3a** is given by the reaction with amines or n-BuLi: in the presence of NEt_3 the allenyl substituted compound **10** is obtained, whereas with n-BuLi the corresponding 1-propynyl substituted derivative **11** can be isolated (scheme 2)[6].

The reaction of **3a** and **10** with $HNEt_2$ leads via a hydroamination type reaction stereoselectively to the heterobutadiene **12** (scheme 2)[6]. Compounds similar to **12** can also be synthesized by the reaction of (R)(R')PCl (R' = CH=CHPh, $CH=CMe_2$, ...) with $Na[Cp(CO)_3Mo]$[2b].



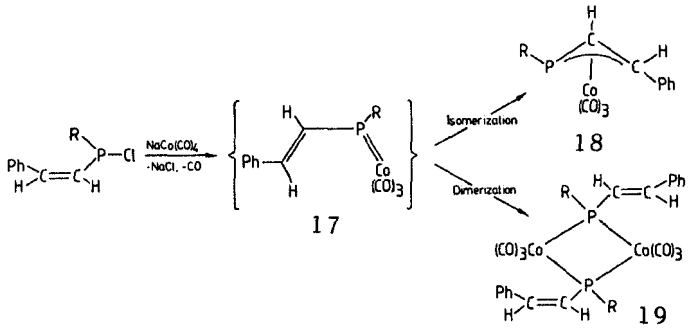
Scheme 2: Propargyl isomerization of **3a**.



Scheme 3: Reaction of **12** with $Fe_2(CO)_9$ and $CoCp(H_2C=CH_2)_2$.

To prove the butadiene analogy of **12**, it was reacted with $Fe_2(CO)_9$ and $CpCo(H_2C{=}CH_2)_2$ as shown in scheme 3[7].
12 yields with $Fe_2(CO)_9$ **13**; **13** decarbonylates at 60 °C to **14**[7]. In this compound the heterobutadiene unit is η^4-side-on coordinated to $Fe(CO)_3$. In a similar way **12** reacts with $CpCo(H_2C{=}CH_2)_2$ to **15** (scheme 3)[7]. In the presence of carbon monoxide **15** forms **16**, a compound, in which only the PMo multiple bond is η^2-side-on bonded to a CpCo(CO) moity[7].

A possible way to synthesize the 1-cobalta-2-phospha-1,3-diene **17** is given in scheme 4[8].



Scheme 4: Isomerization, dimerization of **17**.

(R)(PhHC=CH)PCl reacts with $NaCo(CO)_4$ to yield **18** and **19**[8]. For the formation of **18** and **19** an intermediate like **17** is probably responsible. From **17** the formation of **18** and **19** may easily be explained: isomerization yields **18** and dimerization of the PCo multiple bond **19** (scheme 4)[8].

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