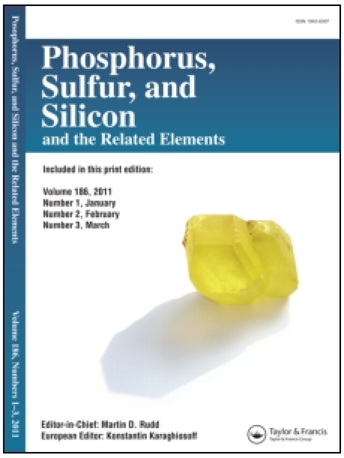

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# Novel Routes to 1,2-Diphosphete and 1,2,4-Triphospholyl π-Complexes

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New specific routes to 1,2-diphosphete-, 1,2,4-triphosphol-, and 1,2,4-triphospholyl-π-complexes are reported, which are based on dichloro-1,2-diphosphetene and 1-stannyl-1,2,4-triphosphol as the heterocyclic educts. Details are given for Sn, Mn, Fe, and Co complexes. ESR-data of paramagnetic 1,2,4-triphospholyl sandwich complexes of Co and Mn proof the absence of degenerate SOMOs in these cases.

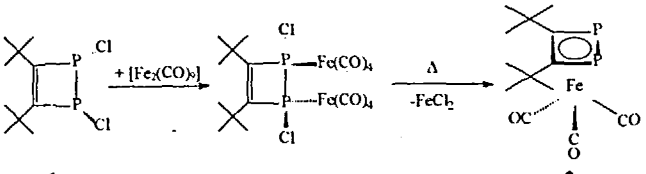
*Keywords:* ESR spectroscopy; P-heterocycles; π-complexes; tin

## INTRODUCTION

Energy and symmetry of the molecular π-orbitals of heterocyclic π-ligands depend distinctly from the number and positions of the hetero atoms within the cycle. As these ligand orbitals determine the frontier orbitals of corresponding π-complexes to a great extend, the same should be true for the complexes. Such a hetero atom effect is much stronger than the influence of substituents on corresponding carbacyclic ligands. We are therefore interested in utilizing it systematically to modify the properties of π-complexes in a targeted way. In this paper we report about our efforts to develop new specific routes to 1,2-diphosphete and 1,2,4-triphospholyl π-complexes, which are designed for a systematic approach to the problem.

### ($\eta^4$-1,2-Diphosphete)M Complexes

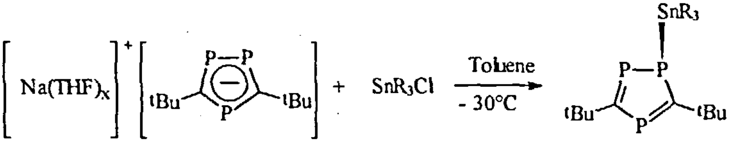
As fas as we know, no specific access to ($\eta^4$-1,2-diphosphete)M complexes has been reported yet. This building block has been obtained only together with its 1,3-isomer and separation of both is difficult. [1] To solve the problem, we followed the route of Pettit, who prepared $\eta^4$-cyclobutadiene iron complexes for the first time, [2] but replaced his educt dichlorocyclobutene by its $P_2$-analogue *trans*-1,2-dichloro-1,2-diphosphetene **1** [3]. At room temperature two $Fe(CO)_4$-fragments are added to the P-atoms of **1** by $Fe_2(CO)_9$ step by step and a binuclear σ-complex is formed in high yield. The dehalogenation of the σ-complex requires elevated temperatures, but it leads directly to the desired product [(3,4-di-*t*-butyl-$\eta^4$-1,2-diphosphete)$Fe(CO)_3$]. **(2)**



1 2

## 1-Stannyl-1,2,4-triphosphol

To the best of our knowledge, no high yield routes are known to prepare 1,2,4-triphospholyl π-complexes effectively. When we tried some reactions of 1,2,4-triphospholyl anions with transition metal complexes as introduced by Nixon et al., [4] we found evidence for competitive redox processes, which may hinder the complex formation reaction severely. However, alternative reactions which utilize P-alkynes [5] are not better in this respect. To diminish the reducing power of 1,2,4-triphospholyl anions, we transferred them into neutral main group metal compounds, with a moderately stable P-M-σ-bond. This approach works effectively, if $Na^+$[3,5-($t$-Bu)$_2$-1,2,4-triphospholyl]$^-$ [6] is allowed to react with $R_3SnCl$ derivatives in THF and P-stannylated 1,2,4-triphosphols (**3a** - **3c**) are formed almost quantitatively. An X-ray study on **3a** proves its diene character with one pyramidal and two planar P-atoms. The same can be deduced from its cyclic addition chemistry with $t$-BuC≡P.



R = Ph (**3a**); Me (**3b**); n-Bu (**3c**)

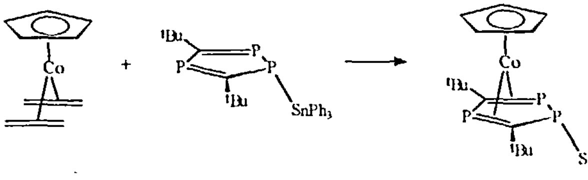
In contrast to the structural features of **3**, [$AB_2X$] spin systems are observed in $^{31}P\{^1H\}$ NMR spectroscopy ($X=^{119}Sn$) at ambient temperatures. They transform into an [ABCX] spin system at - 98°C. We interpret this finding as indicative for a rapid 1,2-shift of the tin atom with $\Delta G^{\neq}$ = 31.5 kJ/mol.

## $\eta^5$-1,2,4-Triphospholyl and $\eta^4$-1,2,4-Triphosphol Complexes

**3a** and **3b** have been proven to be useful starting materials for the preparation of $\eta^5$-1,2,4-triphospholyl complexes if they are reacted with metal educts, which contain anionic leaving groups. This concept works well with $SnCl_2$, $Mn[N(SiMe_3)_2]_2$, or $Mn(CO)_5Br$ for example, leading to ($\eta^5$-1,2,4-triphospholyl)$_2$Sn, (**4**) ($\eta^5$-1,2,4-triphospholyl)$_2$Mn, (**5**) and ($\eta^5$-1,2,4-triphospholyl)Mn(CO)$_3$, (**6**) respectively, all in reasonable (61%) to almost quantitative (98%) isolated yield of pure compounds. The anionic ligand of the metal adds to the leaving $R_3Sn$-group by forming stable compounds $R_3SnX$.

In contrast to all known manganocene derivatives, paramagnetic 17 valence electron (VE) hexaphosphamanganocene **5** is ESR active at room temperature. It exhibits an axially symmetric ESR signal in glassy frozen solutions, which is indicative for a $^2A_1$ electronic ground state for the molecule. Manganocene derivatives with carbacyclic ligands on the other hand, have either a high spin $^6A_1$ or Jahn-Teller active degenerate $^2E_2$ ground states. [7]

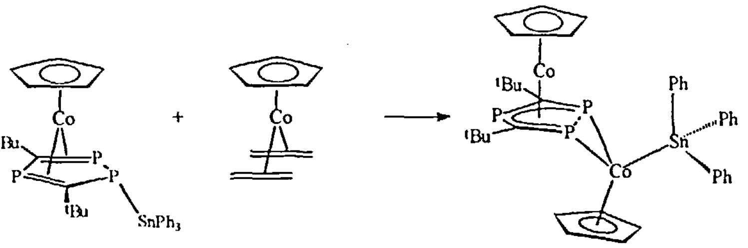
Without an anionic ligand of the metal component, no $\eta^5$-1,2,4-triphospholyl complexes can be formed directly, but **3** may substitute neutral ligands, to yield ($\eta^4$-1-stannyl-1,2,4-triphosphol)M complexes. This takes place if $(C_2H_4)_2(\eta^5\text{-Cp})Co$ and **3a** are reacted in a 1:1 ratio and ($\eta^5$-Cp)($\eta^4$-1-stannyl-1,2,4-triphosphol)Co (**7**) is formed in 80% yield.



**3a** **7**

As one would assume, **7** exhibits an [ABCX] spin system in ${}^{31}P\{{}^1H\}$ NMR, thus the π-complexation of **3a** stops the rapid 1,2-shift of the tin atom.

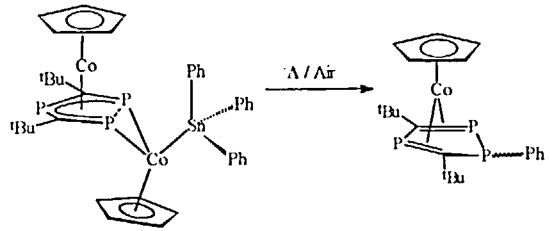
Adding another equivalent of $(C_2H_4)_2(\eta^5\text{-Cp})Co$ to **7** or reacting two moles of $(C_2H_4)_2(\eta^5\text{-Cp})Co$ or more with **3a**, leads to the formation of the extremely slipped 34 VE triple decker sandwich complex **8** in 82% yield.



**7** **8**

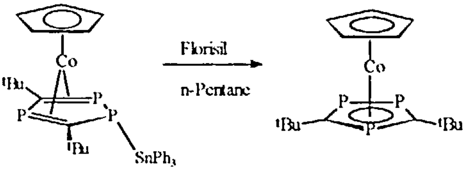
In the solid state the P-Sn-bond is now broken (average distance $P_{(1,2)}$-Sn = 330 pm) and the $Ph_3Sn$-group is transferred to one of the Co-atoms (bonding distance Co-Sn = 250 pm), but as for the free ligand **3a**, an $[AB_2X]$ spin system is observable in ${}^{31}P\{{}^1H\}$ NMR with significant coupling between ${}^{119}Sn$ (X) and the two $P_B$ nuclei (${}^1J_{Sn\text{-}P}$ = 338 Hz). This proves a bonding interaction between the three nuclei in solution, but a P-Sn-P triangle can be ruled out by ${}^{119}Sn$ NMR. No slow exchange limited spectra of **8** have been obtained in solution. The two Co-atoms and their Cp ligands are inequivalent in all NMR spectra. We interpret the combined findings of X-ray crystallography and NMR spectroscopy as indicative for a rapid transfer of the $Ph_3Sn$ group from the Co atom to one of the two bonded P-atoms and back to the same Co-atom. This highly dynamic process is a hint on the reversibility of bond formation and bond breaking P-Sn and Co-Sn.

Exposing solutions of **8** to the air or heating up such samples for some time, leads to a intramolecular reaction, which yields ($\eta^5$-Cp)($\eta^4$-1-phenyl-1,2,4-triphosphol)Co (**9**) in 60% yield and a Cp(stannylene)Co unit leaves the molecule. As no single crystals have been obtained up to now, the position of the phenyl group is not yet clear. As for the other 1,2,4-triphosphol complexes [ABC] spin systems are observed in ${}^{31}P\{{}^1H\}$ NMR.



**8** **9**

If we filtrate ($\eta^4$-1-stannyl-1,2,4-triphosphol)($\eta^5$-Cp)Co 7 through Florisil®, which contains traces of water, the Ph$_3$Sn-group is eliminated without replacement and the paramagnetic 19 VE complex ($\eta^5$-Cp)($\eta^5$-1,2,4-triphospholyl)Co (**10**) is formed.



**7** **10**

As for its 17 VE counterpart hexaphosphamanganocene 5, ESR evidence is found for **10**, that the degeneracy of the SOMO of the Jahn-Teller active cobaltocene derivatives [7] with carbacyclic ligands is broken by the P-atoms of **10**. As hoped for when designing the compound, the SOMO is a non-degenerate MO in this case.

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