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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Transition Metal Substituted Phosphanes: Synthesis, Reactivity and Pyramidal Inversion

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## TRANSITION METAL SUBSTITUTED PHOSPHANES: SYNTHESIS, REACTIVITY AND PYRAMIDAL INVERSION

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Abstract The synthesis of transition metal substituted phosphanes  $C_5H_5(CO)_2M-PPh_2$ ,  $C_5H_5(CO)_2(Me_3P)M-PPh_2$  ( $M = Mo, W$ ) and  $C_5H_5(CO)(Me_3P)FePPhR$  ( $R = Me, Ph$ ) is described as well as their reactivity towards a series of electrophilic and oxidizing reagents.

### INTRODUCTION

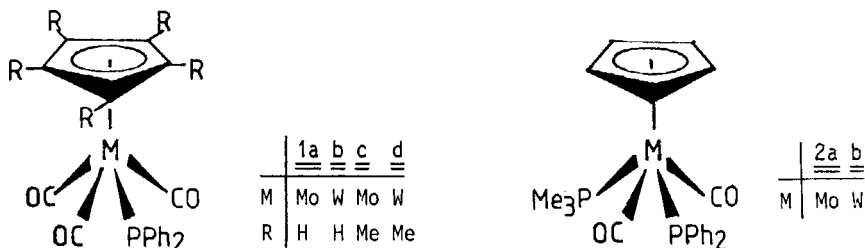
While numerous transition metal substituted arsanes<sup>1</sup> and stibanes<sup>2</sup> are available via the nucleophilic metallation route, the synthesis of the corresponding phosphorus derivatives creates great problems. As a consequence only a few examples of transition metal substituted phosphanes are known.<sup>3</sup> The information about their chemical behaviour is still rather limited.

Therefore we have tried to work out general procedures for their synthesis in the very last time. An access to these species is of special interest, since due to the unusual high donating effect of  $\sigma$ -bonded transition metal moieties like  $C_5R_5(CO)_2Fe$ ,  $C_5R_5(CO)_3M$  ( $M = Cr, Mo, W$ ;  $R = H, Me$ ) they should exhibit pronounced nucleophilic activity at the phosphorus, which should cause unknown reactivities.

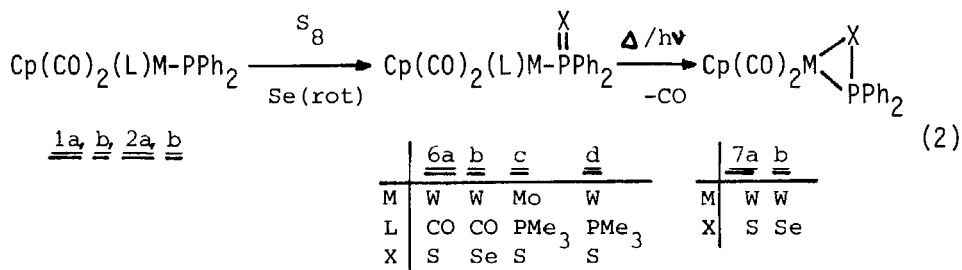
#### 1. Molybdenum and Tungsten Substituted Phosphanes<sup>4</sup>

Phosphanes of the formula  $C_5R_5(CO)_3M-PPh_2$  (1a-d) are available

via nucleophilic metallation of  $\text{Ph}_2\text{PCl}$  with  $\text{Na}[\text{M}(\text{CO})_3\text{C}_5\text{R}_5]$ , in benzene.

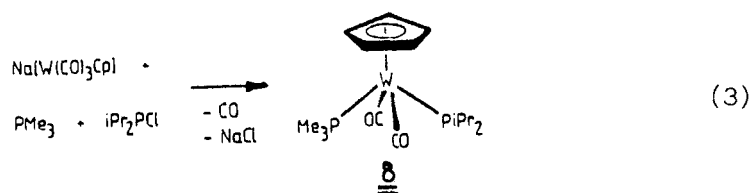


In refluxing benzene 1a, b convert in a rather complicated reaction to the dinuclear complexes  $(\mu^2\text{-H})(\mu^2\text{-PPh}_2)[\text{Cp}(\text{CO})_2\text{M}]_2$ , which is believed to involve the double bonded species  $\text{Cp}(\text{CO})_2\text{-M=PPh}_2$ . Interaction of 1a, b with  $\text{Me}_3\text{P}$  yields the phosphanes 2a, b with CO elimination, which are obtained as the pure trans-isomer and exhibit an unusual high Lewis basicity at the trivalent phosphorus atom. This property allows rapid quarternization with  $\text{MeI}$ ,  $\text{MeC(O)Cl}$  or oxidation with molecular halogen to the salt like species  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})\text{M-PPh}_2\text{R}]\text{X}$  ( $\text{R} = \text{Me}$ ,  $\text{X} = \text{I}$  (3a);  $\text{R} = \text{MeC(O)}$ ,  $\text{X} = \text{Cl}$  (3b)) and  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})\text{M-PPh}_2\text{X}]\text{X}$  ( $\text{X} = \text{Br}$  (4a),  $\text{I}$  (4b)). The treatment of 2a, b with the Lewis acids  $\text{BH}_3$  and  $\text{BF}_3$  leads to the formation of stabile adducts  $\text{Cp}(\text{CO})_2\text{-(Me}_3\text{P})\text{M-PPh}_2\text{-BX}_3$  (5a-d). Sulfur or selenium oxidizes 1a, b, 2a, b to the transition metal substituted sulfides and selenides 6a-d.



6a, b yields the three membered metallacycles 7a, b on photolysis or thermal treatment.

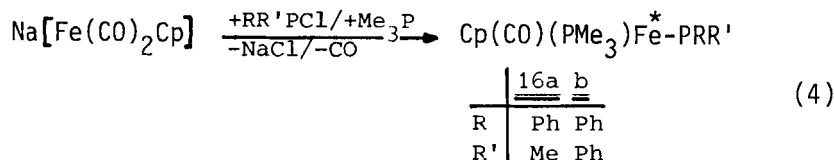
The only phosphane bearing alkyl groups besides an  $\eta^5$ -bonded transition metal ligand obtained so far, is 8, which is formed in an one pot reaction according to eq. 3 together with the salts  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})_2\text{W}][\text{W}(\text{CO})_3\text{Cp}]$  (9) and  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})(i\text{Pr}_2\text{PH})\text{W}][\text{W}(\text{CO})_3\text{Cp}]$  (10).<sup>5</sup>



According to the  $\Delta G^\ddagger$  value of 14.4 kcal/mol, determined for 8, the transition metal group lowers the barrier of inversion extraordinarily. In order to exclude, that an "inverse pseudorotation" at the metal centre is responsible for the dynamic behaviour, the tetravalent derivatives  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})\text{M}-\text{P}i\text{Pr}_2(\text{R})]\text{Hal}$  ( $\text{R} = \text{H}, \text{Me}$ ) (11a, b),  $\text{Cp}(\text{CO})_3\text{W}-\text{P}i\text{Pr}_2(\text{S})$  (12) and  $[\text{Cp}(\text{CO})_2(\text{Me}_3\text{P})\text{W}-\text{P}i\text{Pr}_2\text{Br}]\text{Br}_3$  (13), are prepared from 8 by protonation, alkylation, sulfur or bromine addition. 11-13 show no temperature dependent n. m. r. spectra.

## 2. Iron Substituted Phosphanes

The interaction of the extremely strong nucleophilic anion  $\text{Cp}(\text{CO})_2\text{Fe}^-$  with the chlorophosphane  $\text{Ph}_2\text{PCl}$  or  $\text{PhMePCl}$  in the presence of  $\text{Me}_3\text{P}$  offers a simple route to the preparation of the phosphanes 14a, b containing a chiral transition metal group.



14a, b, which have in addition a chiral phosphorus atom are obtained as a 1 : 1 mixture of diastereomers (RR/SS; RS/SR). This fact is clearly established in the  $^1\text{H}$  and the  $^{31}\text{P}$  n. m. r. spectrum. Quarternization with  $\text{PhCH}_2\text{Br}$  or oxidative addition of sulfur yields diastereomers of  $[\text{Cp}(\text{CO})(\text{Me}_3\text{P})\text{Fe}^*\text{-P}^*\text{Ph}(\text{Me})\text{CH}_2\text{Ph}]\text{Br}$  (15) and  $\text{Cp}(\text{CO})(\text{Me}_3\text{P})\text{Fe}^*\text{-P}^*\text{Ph}(\text{Me})\text{S}$  (16).

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