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

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### Reaction of Methylene Bridged Diphosphines $R_2P-CH_2-PRH$ AND $RHP-CH_2-PRH$ ( $R = Me, Pr^i, Bu^t, CH_2-Ph$ ) with Transition Metal Carbonyls

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## REACTION OF METHYLENE BRIDGED DIPHOSPHINES

$R_2P-CH_2-PRH$  AND  $RHP-CH_2-PRH$  ( $R = Me, Pr^i, Bu^t, CH_2-Ph$ ) WITH TRANSITION METAL CARBONYLS

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**Abstract** The PH-functional methylene bridged diphosphines  $R_2P-CH_2-PRH$  and  $RHP-CH_2-PRH$  have been synthesized using  $Cl_2P-CH_2-PCl_2$  as a starting material. On reaction with  $Fe_2(CO)_9$  oxidative addition and cleavage of the P-C-P-skeleton occur yielding cluster compounds, e.g.  $(CO)_9Fe_3(RR'P-CH_2-PR)H$  ( $R = Me, Pr^i, Bu^t, CH_2-Ph, R' = R$  or  $H$ ) or  $(CO)_9Fe_3(\mu_3PR)(\mu_2PMeR)H$ .

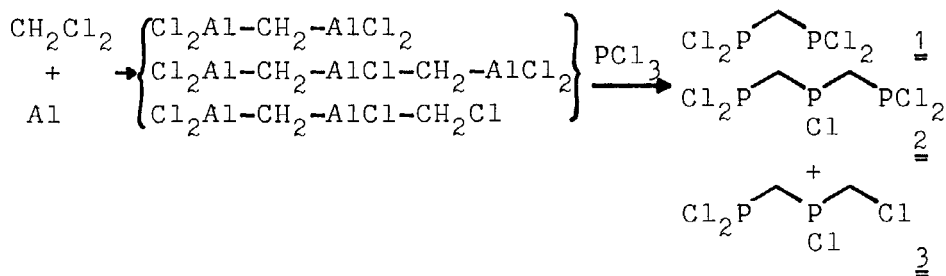
## INTRODUCTION

Bidentate phosphines containing the P-C-P-skeleton may lock together two metal atoms in close proximity and hence promote reactions involving the two metal centres.<sup>1</sup> This has been shown for a large number of Pd-, Pt-, Rh- and Fe-complexes of bis(diphenylphosphino)methane (dpm), e.g.  $X_nM(dpm)_2MX_n$  and  $(CO)_4Fe-dpm-Fe(CO)_4$ <sup>2</sup> or  $(CO)_3Fe(\mu dpm)(\mu CO)Fe(CO)_3$ .<sup>3</sup>

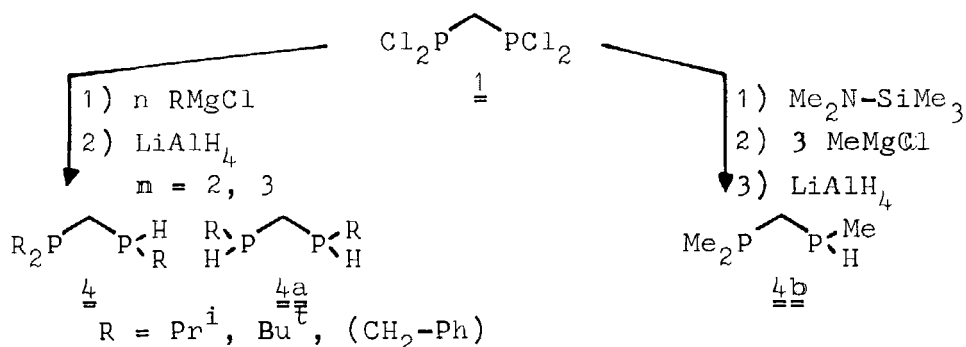
## SYNTHESES OF THE LIGANDS $RR'P-CH_2-PRH$ ( $R' = R, H$ )

The chlorophosphine  $Cl_2P-CH_2-PCl_2$ <sup>4</sup> (1) may be obtained in fair yields (30 - 40 %) by a procedure given by Novikova, Prishchenko and Lutsenko using cheap starting materials ( $PCl_3$ , Al and  $CH_2Cl_2$ ).

In addition to 1 we could isolate the interesting phosphines 2 and 3 from the reaction mixture.<sup>5</sup>



Compound 1 proved to be a versatile starting material for a number of methylene bridged phosphines, e.g.



The compounds were analytically identified and characterized by their  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{13}\text{C}$ -NMR spectra.

### REACTIONS WITH $\text{Fe}_2(\text{CO})_9$

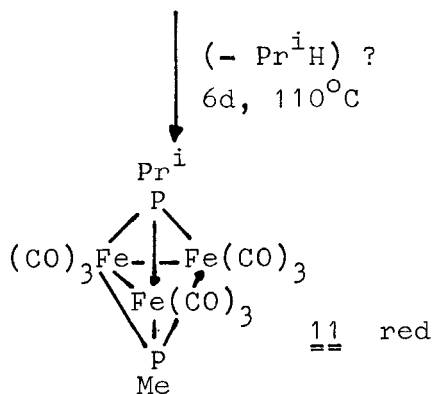
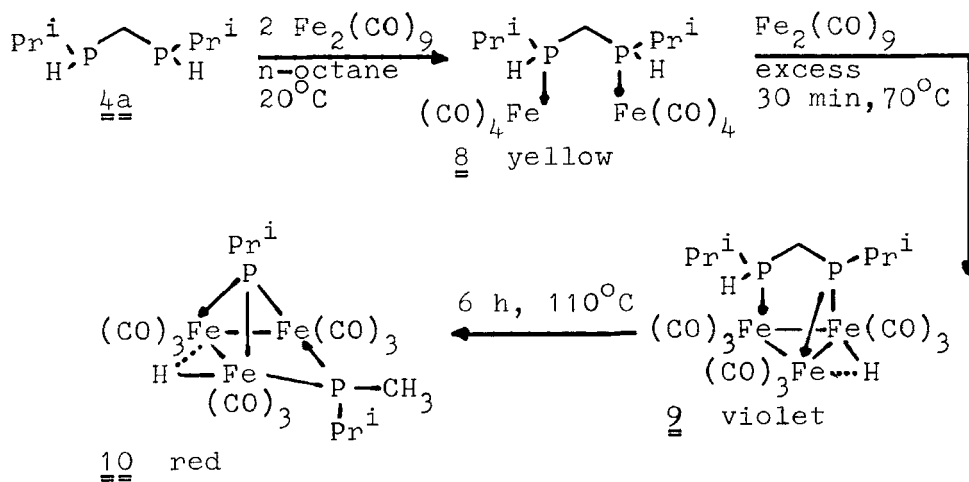
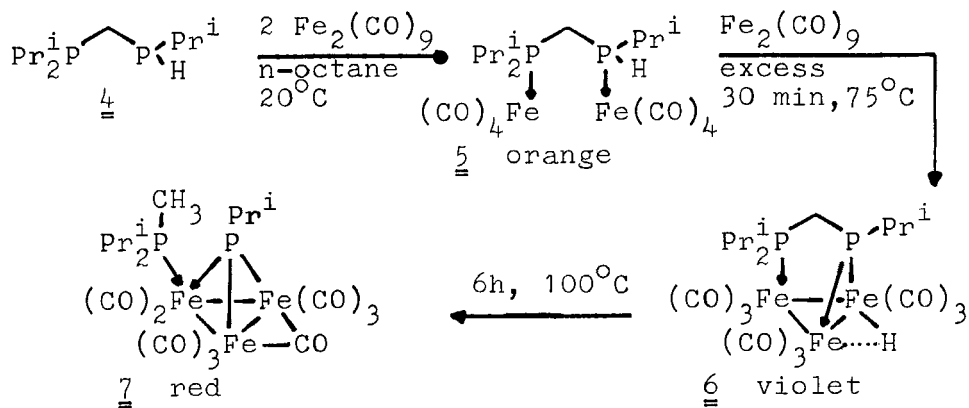
The reactivity pattern of these PH-functional phosphines is determined by

a) their bidentate character, b) the reactivity of the PH-bonds, c) phosphinidene formation with cleavage of the P-C-P-skeleton.

The combination of these reactions offers a new and interesting way for the synthesis of cluster compounds.

This is shown by the reaction of  $\text{Pr}_2^i\text{P-CH}_2\text{-PPr}^i\text{H}$  and  $\text{HPr}^i\text{P-CH}_2\text{-PPr}^i\text{H}$  with  $\text{Fe}_2(\text{CO})_9$ .

The structure of the compounds thus obtained will be discussed on basis of their  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectra, mass spectra and IR-spectra.



The crystal structure of cluster 10 shows the presence of a  $\mu_3$ -PPr<sup>i</sup> and a  $\mu_2$ -PPr<sup>i</sup>Me group.

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