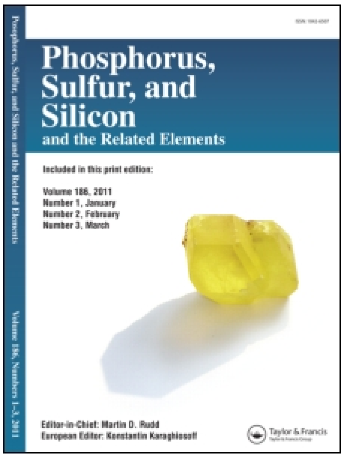

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Reaction of Methylene Bridged Diphosphines $R_2P\text{-}CH_2\text{-}PRH$ AND $RHP\text{-}CH_2\text{-}PRH$ (R = Me, Pr^i, Bu^t, $CH_2\text{-}Ph$) with Transition Metal Carbonyls

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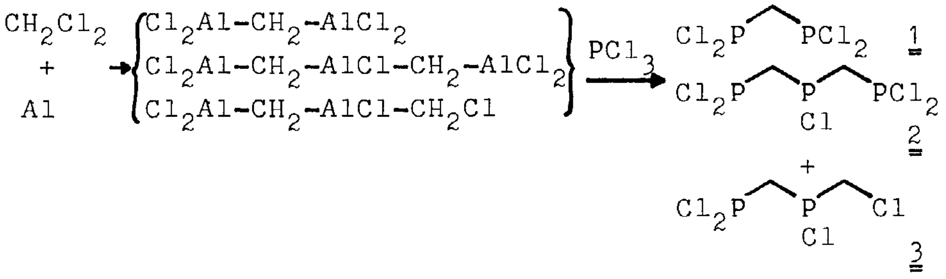
Abstract The PH-functional methylene bridged diphosphines R_2P-CH_2-PRH and $RHP-CH_2-PHR$ have been synthesized using $Cl_2P-CH_2-PCl_2$ as a starting material. On reaction with $Fe_2(CO)_9$ oxidative addition and cleavage of the P-C-P-skeleton occur yielding cluster compounds, e.g. $(CO)_9Fe_3(RR'P-CH_2-PR)H$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

INTRODUCTION

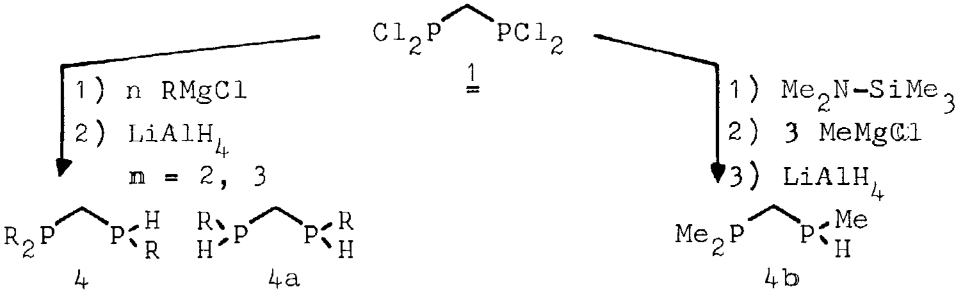
Bidentate phosphines containing the P-C-P-skeleton may lock together two metal atoms in close proximity and hence promote reactions involving the two metal centres.[1] This has been shown for a large number of Pd-, Pt-, Rh- and Fe-complexes of bis(diphenylphosphino)methane (dpm), e.g. $X_nM(dpm)_2MX_n$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

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

The chlorophosphine $Cl_2P-CH_2-PCl_2$[4] (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.[5]



Compound $\underline{\underline{1}}$ proved to be a versatile starting material for a number of methylene bridged phosphines, e.g.



R = Pr^i, Bu^t, (CH_2-Ph)

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

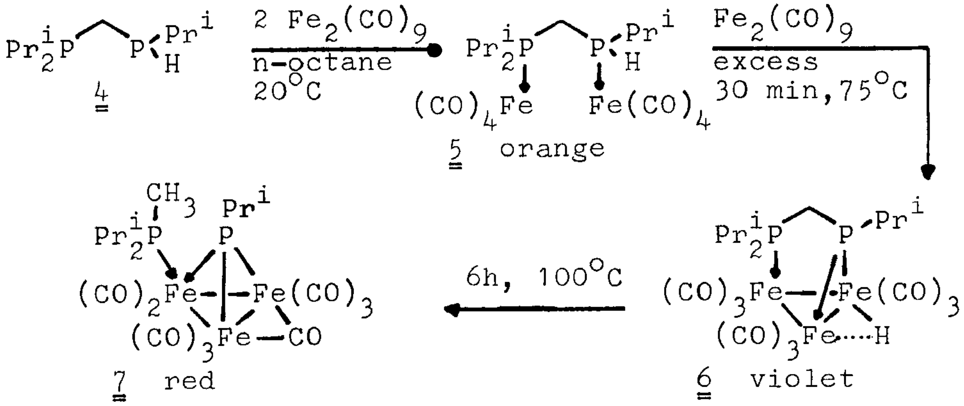
REACTIONS WITH $Fe_2(CO)_9$

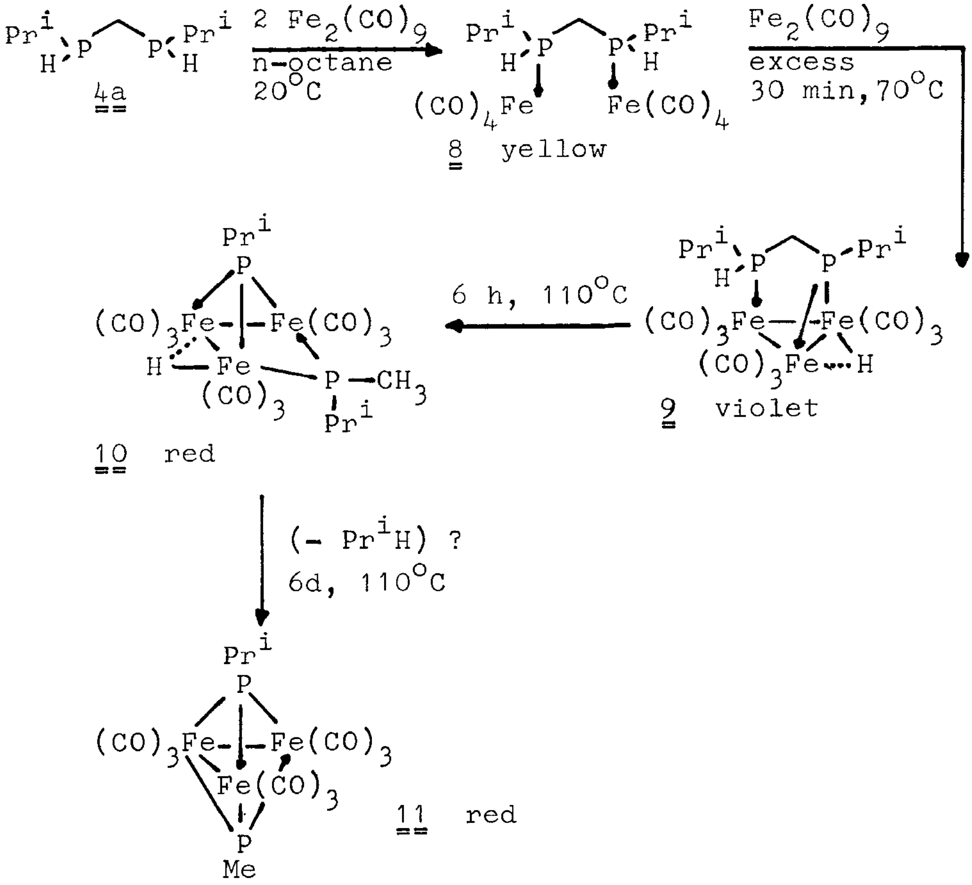
The reactivity pattern of these PH-functional phosphines is determined by

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 $Pr^i_2P-CH_2-PPr^iH$ and $HPr^iP-CH_2-PPr^iH$ with $Fe_2(CO)_9$.

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


4
2 Fe2(CO)9
n-octane
20°C
5 orange
Fe2(CO)9
excess
30 min,75°C
6 violet
6h, 100°C
7 red


4a
2 Fe2(CO)9
n-octane
20°C
8 yellow
Fe2(CO)9
excess
30 min,70°C
9 violet
6 h, 110°C
10 red
(- PriH) ?
6d, 110°C
11 red

The crystal structure of cluster 10 shows the presence of a μ_3-PPr^i and a μ_2-PPr^{i}Me group.

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