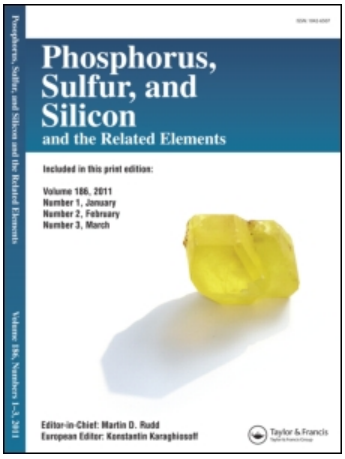

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Me_5C_5: A Versatile Ligand in Phosphorus Chemistry

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ME_5C_5: A VERSATILE LIGAND IN PHOSPHORUS CHEMISTRY

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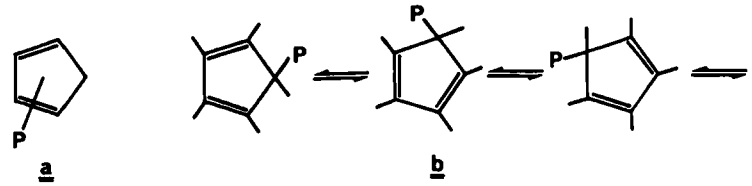
Abstract Pentamethylcyclopentadienyl (pcp) phosphorus compounds with coordination number 2, 3, and 4 at phosphorus are described concentrating on their differing fluxional behavior (sigmatropic rearrangements). The pcp-substituted diphosphene allows for the first time a substitution chemistry at the P=P unit.

The unique properties of the pentamethylcyclopentadienyl (pcp) ligand open new fields in main-group chemistry. Here we report on some recent results from phosphorus chemistry.

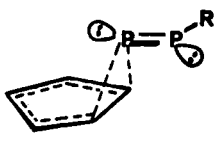
I) SYNTHESIS AND FLUXIONAL BEHAVIOR OF PCP-PHOSPHORUS COMPOUNDS

Several pcp phosphorus compounds have been synthesized by classical methods. Whereas cyclopentadienylphosphanes a exist as vinylic isomers, the pcp phosphanes b are present only in form of their allylic isomers, thus capable for degenerate sigmatropic rearrangements.

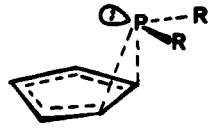


a b

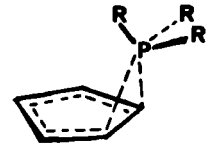
Surprisingly great differences in fluxionality have been observed for these compounds. The activation energies for sigmatropic processes lie between $\lesssim$ 5 and $\gtrsim$ 30 kcal/mol, i. e. the relevant molecules have to be classified within a wide range from highly fluxional to rigid (see Table 1). E_A-values depend I) on the coordination number at phosphorus and II) on the further ligands bound to the phosphorus atom. The experimental data can be correlated with relevant ground- and transition-state energies. Thus, in the diphosphene PcpP=PPcp the very low E_A-value can be explained with the assumption of a transition-state A, which is stabilized by π(pcp)-π^*(P=P) interaction. The large differences in the E_A-values of pcp-PR_2 compounds can be rationalized by assuming transition-state geometries B, where mesomeric effects in the (π-allyl-type) PR_2 unit are possible. Differences in the E_A-values of comparable open-chain and cyclic pcp-phosphanes can be correlated with differing ground-state energies of these molecules. Finally, no strong ligand effects are expected for compounds with coordination number 4 at phosphorus (see transition state C).



A



B



C

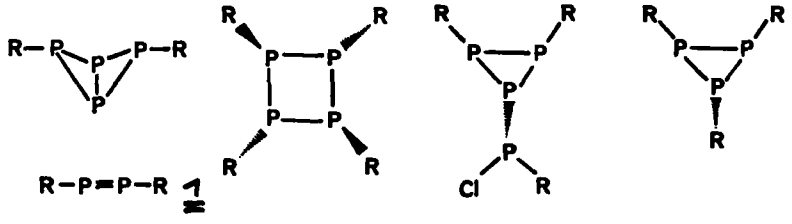
TABLE 1 Activation Energies for 1,2 Element--Shifts in Pentamethylcyclopentadienyl Compounds of Phosphorus

Compound,	E_A(kcal/mol)	Compound,	E_A(kcal/mol)
Me_5C_5-P=PC_5Me_5	<8[a]	Me_5C_5-P(OMe)(OMe)	21.2±0.4
Me_5C_5-P(Me)(Me)	23.0±0.5	Me_5C_5-P(SMe)(SMe)	17.5±1.3
Me_5C_5-P(Me)(Cl)	16.4±1.1	Me_5C_5-P(NMe_2)(NMe_2)	19.0±1.2
Me_5C_5-P(^{t}Bu)(Cl)	21.3±1.5	Me_5C_5-P(O,O)	16.3±1.6
Me_5C_5-P(H)(H)	31.3±1.8	Me_5C_5-P(S,S)	15.2±0.5
Me_5C_5-P(F)(F)	16.7±0.7	Me_5C_5-P(NMe,NMe)	6.2±0.6
Me_5C_5-P(Cl)(Cl)	12.0±1.6	Me_5C_5-P(O,O)-C$_6$H$_4$	12.3±0.8
Me_5C_5-P(Br)(Br)	5.2±3.1	Me_5C_5-P$Me_3^+J^-$	>35[a]
		Me_5C_5-P(S)R_2	>35[a]
		Me_5C_5-PR_2·Cr(CO)$_5$	>35[a]

a) estimated value

II) SYNTHESIS, STRUCTURE AND CHEMISTRY OF A DIPHOSPHENE WITH PCP-LIGANDS

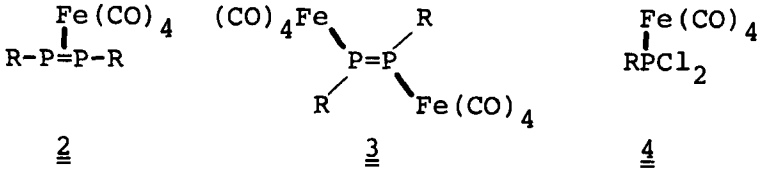
Reduction of pcp-dihalophosphanes $Me_5C_5PHal_2$ (Hal = Cl, Br) with alkali metal naphthalenides leads to the following compounds:



$R = Me_5C_5$

The reactivity of the phosphorus-carbon σ-bond in these molecules can be used for substitution reactions. Here we report on the substitution chemistry of 1. In the reaction of 1 with nucleophiles (lithiumalkyls, lithiumamides) mixed substituted diphosphenes PcpP=PR and disubstituted diphosphenes RP=PR can be isolated or characterized spectroscopically.

Reaction of 1 with $Fe_2(CO)_9$ leads to the iron complex 2; reaction of pcp-dichlorophosphane with $Na_2Fe(CO)_4$ yields compound 1 and a mixture of the iron complexes 2, 3 and 4.



2 3 4