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Me_5C_5 : A Versatile Ligand in Phosphorus Chemistry

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ME₅C₅: A VERSATILE LIGAND IN PHOSPHORUS CHEMISTRY

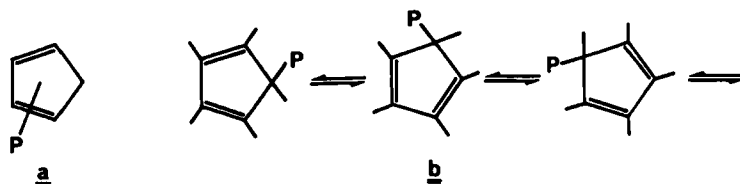
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Abstract Pentamethylcyclopentadienyl (pcp) phosphorus compounds with coordination number 2, 3, and 4 at phosphorus are described concentrating on their differing fluxional behavior (sigmatropic rearrangements). The pcp-substituted diphosphene allows 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.



Surprisingly great differences in fluxionality have been observed for these compounds. The activation energies for sigmatropic processes lie between ≤ 5 and ≥ 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 $\pi(\text{pcp})-\pi^*(\text{P=P})$ 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).

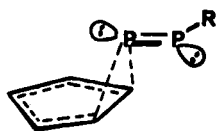
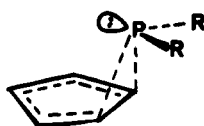
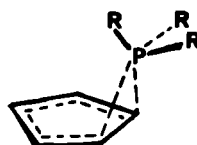












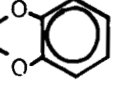

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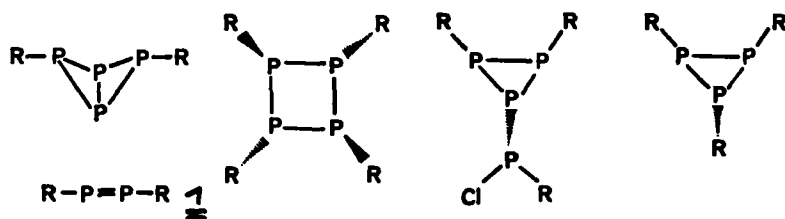
TABLE 1 Activation Energies for 1,2 Element-Shifts in Pentamethylcyclopentadienyl Compounds of Phosphorus

Compound, E _A (kcal/mol)		Compound, E _A (kcal/mol)	
Me ₅ C ₅ -P=PC ₅ Me ₅	<8 ^a	Me ₅ C ₅ -P 	21.2±0.4
Me ₅ C ₅ -P 	23.0±0.5	Me ₅ C ₅ -P 	17.5±1.3
Me ₅ C ₅ -P 	16.4±1.1	Me ₅ C ₅ -P 	19.0±1.2
Me ₅ C ₅ -P 	21.3±1.5	Me ₅ C ₅ -P 	16.3±1.6
Me ₅ C ₅ -P 	31.3±1.8	Me ₅ C ₅ -P 	15.2±0.5
Me ₅ C ₅ -P 	16.7±0.7	Me ₅ C ₅ -P 	6.2±0.6
Me ₅ C ₅ -P 	12.0±1.6	Me ₅ C ₅ -P 	12.3±0.8
Me ₅ C ₅ -P 	5.2±3.1	Me ₅ C ₅ -PMe ₃ ⁺ J ⁻	>35 ^a
		Me ₅ C ₅ -P(S)R ₂	>35 ^a
		Me ₅ C 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 $\text{Me}_5\text{C}_5\text{PHal}_2$ (Hal = Cl, Br) with alkali metal naphthalenides leads to the following compounds:



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 $\text{PcpP}=\text{PR}$ and disubstituted diphosphenes $\text{RP}=\text{PR}$ can be isolated or characterized spectroscopically.

Reaction of 1 with $\text{Fe}_2(\text{CO})_9$ leads to the iron complex 2; reaction of pcp-dichlorophosphane with $\text{Na}_2\text{Fe}(\text{CO})_4$ yields compound 1 and a mixture of the iron complexes 2, 3 and 4.

