

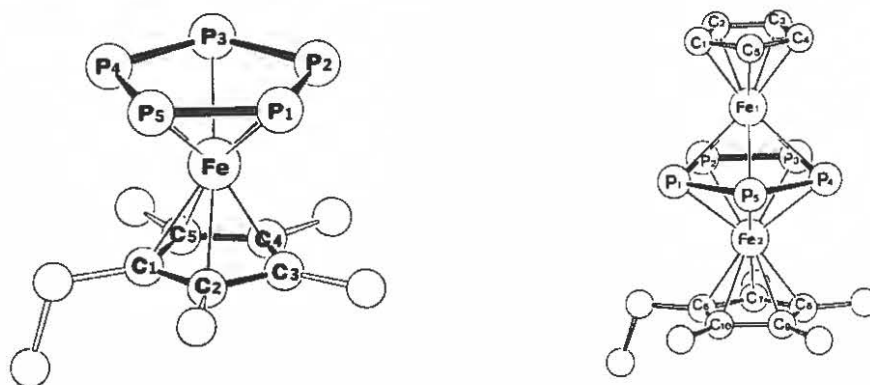
Cyclo-P₅⁻ : An Analogue of Cp⁻

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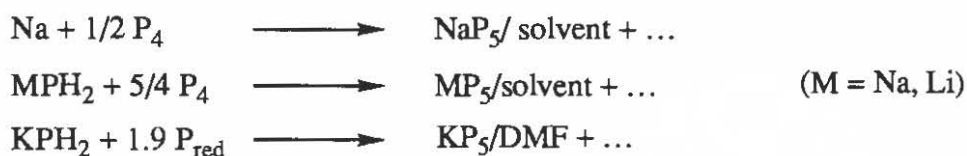
Literature seminar

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The cyclopentadienyl (Cp⁻) ligand has played a vital role in the development of organo-metallic chemistry [1]. However, its analogue, cyclo-P₅⁻ had not been known until last few years. In early 1984, theorists predicted the existence of cyclo-P₅⁻ by MNDO calculation [2]. Two years later, P₅⁻ was observed in the negative ion photoelectron spectrum of red phosphorus [3]. The first complex containing stabilized cyclo-P₅⁻, (η⁵-Cp*)Cr(η⁵-P₅)Cr(η⁵-Cp*), was synthesized in 1986 by O. J. Scherer [4]. In the following year, the synthesis of pentaphosphaferrocene, (η⁵-P₅)Fe(η⁵-Cp*), was reported [5]. During the same period of time, the preparations of cyclo-P₅⁻ alkali-metal salts (Li, Na) in solution were reported by M. Baudler [6]. These combined efforts have dramatically accelerated the chemistry involving cyclo-P₅⁻ ligand.



The preparations of cyclo-P₅⁻ alkali-metal salts (K, Na, Li) in solution have been carried out through three methods [6-9]:



The stability of the resulted MP₅ solution is solvent dependent as well as metal dependent. KP₅/THF solution has shown the highest stability. ³¹P NMR spectra of MP₅ salts showed a sharp singlet. Neither splitting nor broadening of the singlet was observed at low temperature, implying that all five phosphorus atoms are equivalent and unsubstituted. Other NMR studies (⁷Li, ²³Na) proved the ionic property of the MP₅ salts. The UV spectra indicated the aromatic nature of cyclo-P₅⁻.

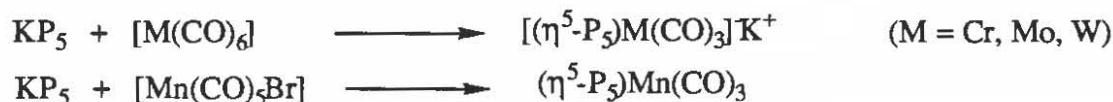
Extended Hückel calculations [10] showed that cyclo-P₅⁻ has the same number of π-bonding and π-antibonding orbitals as Cp⁻. However, the HOMO in cyclo-P₅⁻ are occupied by lone pairs of electrons of P atoms, and the π-bonding orbitals in cyclo-P₅⁻ are higher in energy than that of Cp⁻. As a result, cyclo-P₅⁻ was predicted to be a better π-donor, and to be able to use its lone pairs of electrons on P atoms for further coordination.

Cothermolysis of [(η⁵-Cp*)Fe(CO)₂]₂ with white phosphorus yielded the first sandwich complex (η⁵-P₅)Fe(η⁵-Cp*) in 1987 [5]. The same method has been used to prepare the ruthenium analogue [11], and the iron double sandwich complex [13]. In contrast, another synthetic approach has been used to afford the same complex by using LiP₅ as the direct cyclo-

P_5^- source with $LiCp^*$ and $FeCl_2$ [7]. The cyclo- P_5^- in these complexes has been proved to be a planar, six-electron, η^5 -ligand. The P-P bond distance is between a P-P single bond and a P=P double bond [11, 12]. Beside being a η^5 -ligand, cyclo- P_5^- can use the lone pairs of electrons on P atoms for further coordination. The examples are $[(Cr(CO)_5)_2(\eta^5-P_5)Fe(\eta^5-Cp^*)]$ and $[(Mn(CO)_2(\eta^5-Cp))_n(\eta^5-P_5)Fe(\eta^5-Cp^*)]$ ($n = 1-4$) [14].

Similar to Cp^- complex, cyclo- P_5^- complex can also stack to form multi-decker complex. So far, the following triple-decker complexes are known: $[(\eta^5-Cp^*)Cr(\eta^5-P_5)Cr(\eta^5-Cp^*)]$ [4], and $[(\eta^5-Cp)Fe(\eta^5-P_5)Fe(\eta^5-C_5Me_4R)]PF_6$ ($R = Me, Et$) [14]. One double-triple-decker complex: $[Me_2Si\{(\eta^5-C_5Me_4)Fe(\mu, \eta^5:5-P_5)Fe(\eta^5-Cp)\}_2]^{2+}2PF_6^-$ was also synthesized recently [13]. Cr compound is the first cyclo- P_5^- complex. It is a neutral, mix-valenced (d^4/d^5) species. The paramagnetic nature of this complex was revealed by its 1H NMR, EPR spectrum and magnetic susceptibility [16], which could be explained by its molecular orbital diagram [15]. The cyclovoltammetric study showed that the 27 valence electron chromium complex can be either reversibly reduced to a 28 valence electron anion ($E_{red} = -0.97$ V) or oxidized to a 26 valence electron cation ($E_{ox} = 0.07$ V). The Fe complex is a diamagnetic cation with 30VE. Its molecular structure showed that the bridging ligand P_5^- remains the same structure feature as that of the starting sandwich complex.

Half-sandwich complexes involving cyclo- P_5^- ligand were made by reacting $M'P_5$ salts ($M' = K, Li$) with transition-metal carbonyl complex [17].



The success in the preparation of half-sandwich complex is mainly due to the availability of the "surprisingly stable" cyclo- P_5^- source: KP_5 [9]. The lower CO vibrational frequencies in complex $(\eta^5-P_5)Mn(CO)_3$ than those in complex $(\eta^5-Cp)Mn(CO)_3$ [18] was attributed to the stronger π -donating nature of cyclo- P_5^- . This observation supported the prediction from MO calculation.

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