Cyclo-P\textsubscript{5}\textsuperscript{-} : An Analogue of Cp\textsuperscript{-}

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The cyclopentadienyl (Cp\textsuperscript{-}) ligand has played a vital role in the development of organo-metallic chemistry [1]. However, its analogue, cyclo-P\textsubscript{5}\textsuperscript{-} had not been known until last few years. In early 1984, theorists predicted the existence of cyclo-P\textsubscript{5}\textsuperscript{-} by MNDO calculation [2]. Two years later, P\textsubscript{5}\textsuperscript{-} was observed in the negative ion photoelectron spectrum of red phosphorus [3]. The first complex containing stabilized cyclo-P\textsubscript{5}\textsuperscript{-}, (\(\eta^5\text{-}\text{Cp}^*\))Cr(\(\eta^5\text{-}\text{P}_5\))Cr(\(\eta^5\text{-}\text{Cp}^*\)), was synthesized in 1986 by O. J. Scherer [4]. In the following year, the synthesis of pentaphosphaferrocene, (\(\eta^5\text{-}\text{P}_5\))Fe(\(\eta^5\text{-}\text{Cp}^*\)), was reported [5]. During the same period of time, the preparations of cyclo-P\textsubscript{5}\textsuperscript{-} alkali-metal salts (Li, Na) in solution were reported by M. Baudler [6]. These combined efforts have dramatically accelerated the chemistry involving cyclo-P\textsubscript{5}\textsuperscript{-} ligand.

The preparations of cyclo-P\textsubscript{5}\textsuperscript{-} alkali-metal salts (K, Na, Li) in solution have been carried out through three methods [6-9]:

\[
\begin{align*}
\text{Na} + \frac{1}{2} \text{P}_4 & \quad \rightarrow \quad \text{NaP}_5/\text{solvent} + \ldots \\
\text{MPH}_2 + \frac{5}{4} \text{P}_4 & \quad \rightarrow \quad \text{MP}_5/\text{solvent} + \ldots \\
\text{KPH}_2 + 1.9 \text{P}_{\text{red}} & \quad \rightarrow \quad \text{KP}_5/\text{DMF} + \ldots 
\end{align*}
\]

The stability of the resulted MP\textsubscript{5} solution is solvent dependent as well as metal dependent. KP\textsubscript{5}/THF solution has shown the highest stability. \(^{31}\text{P}\) NMR spectra of MP\textsubscript{5} 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 (\(^{7}\text{Li}, ^{23}\text{Na}\)) proved the ionic property of the MP\textsubscript{5} salts. The UV spectra indicated the aromatic nature of cyclo-P\textsubscript{5}\textsuperscript{-}.

Extended Hückel calculations [10] showed that cyclo-P\textsubscript{5}\textsuperscript{-} has the same number of \(\pi\)-bonding and \(\pi\)-antibonding orbitals as Cp\textsuperscript{-}. However, the HOMO in cyclo-P\textsubscript{5}\textsuperscript{-} are occupied by lone pairs of electrons of P atoms, and the \(\pi\)-bonding orbitals in cyclo-P\textsubscript{5}\textsuperscript{-} are higher in energy than that of Cp\textsuperscript{-}. As a result, cyclo-P\textsubscript{5}\textsuperscript{-} was predicted to be a better \(\pi\)-donor, and to be able to use its lone pairs of electrons on P atoms for further coordination.

Cothermolysis of \([(\eta^5\text{-}\text{Cp}^*)\text{Fe(\text{CO})}_2]_2\) with white phosphorus yielded the first sandwich complex \((\eta^5\text{-}\text{P}_5)\text{Fe(\eta^5\text{-}\text{Cp}^*)}\) 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 LiP\textsubscript{5} as the direct cyclo-
The cyclo-P$_5^-$ in these complexes has been proved to be a planar, six-electron, σ$_g$-ligand. The P-P bond distance is between a P-P single bond and a P=P double bond [11, 12]. Besides being a σ$_g$-ligand, cyclo-P$_5^-$ can use the lone pairs of electrons on P atoms for further coordination. The examples are [[Cr(CO)$_5$]$_2$(η$_5$-P$_5$)Fe(η$_5$-Cp*)] and [[Mn(CO)$_2$(η$_5$-Cp)]$_n$(η$_5$-P$_5$)Fe(η$_5$-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: [(η$_5$-Cp*)Cr(η$_5$-P$_5$)Cr(η$_5$-Cp*)] [4], and [(η$_5$-Cp)Fe(η$_5$-P$_5$)Fe(η$_5$-C$_5$Me$_4$R)]PF$_6$ (R = Me, Et) [14]. One double-triple-decker complex: [Me$_2$Si{(η$_5$-C$_5$Me$_4$)Fe(μ,P$_5$)Fe(η$_5$-C$_5$Me$_5$)}]$_2$PF$_6$ 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 $^1$H 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 MP$_5^-$ salts (M' = K, Li) with transition-metal carbonyl complex [17].

$$\begin{align*}
\text{KP}_5 + [\text{M(CO)}_6] & \rightarrow [[\eta_5^5\text{-P}_5]\text{M(CO)}_3]\text{K}^+ \\
\text{KP}_5 + [\text{Mn(CO)}_3\text{Br}] & \rightarrow (\eta_5^5\text{-P}_5)\text{Mn(CO)}_3
\end{align*}$$

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 (η$_5$-P$_5$)Mn(CO)$_3$ than those in complex (η$_5$-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.

References


16. Bronger, W., unpublished results
