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Preliminary communication

Novel synthesis of di- and tri-phosphollide ions and their ferrocene analogues

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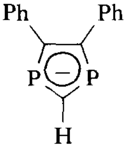
Abstract

The preparations of di- and tri-phosphollide ions $P_3C_2R_2^-$, $P_3C_2RR'^-$, $P_2C_3R_3^-$, $P_2C_3R_2R'^-$, $P_2C_3RR_2'^-$, $P_2C_3'R_3'$ ($R = {}^tBu$, $R = {}^iPr$) and their pentaphospha-ferrocene analogues are described.

The recent publication by Mathey and co-workers [1] of a new synthetic route to the second known example of a 1,3-diphosphollide anion $P_2C_3HPh_2^-$ (I), prompts us to report the unusual synthesis of several new ions of this structural type, and their ready conversion into the corresponding pentaphospha-ferrocenes.

Previously we have described the direct synthesis of a mixture of the di- and tri-phosphollide ions $(P_2C_3{}^tBu_3)^-$ (II), and $(P_3C_2{}^tBu_2)^-$ (III), by the direct reaction between ${}^tBuC{\equiv}P$ and sodium amalgam in monoglyme. [2] Interestingly, we now find that when a mixture of ${}^tBuC{\equiv}P$ and ${}^iPrC{\equiv}P$ [3] is treated with sodium in monoglyme all possible nine phosphollide ring systems II → X shown below are formed as evidenced by ${}^{31}P\{{}^1H\}$ NMR spectroscopic monitoring of the reaction mixture (see Fig. 1). The resonances of the ions II and III are already known [1] while those of IV and V can be identified when ${}^iPrC{\equiv}P$ alone is treated with Na in monoglyme. The resonances of other individual di- and tri-phosphollide ions can be readily assigned if the assumption ion is made that the presence of a ${}^tBu$ group causes a greater downfield shift than its ${}^iPr$ counterpart. The ring systems thus represent examples of $[AB_2]$ (III, V); $[ABC]$ (VI); $[A_2]$ (II, IV, IX and X); and $[AB]$ (VII, VIII) nuclear spin-systems (A, B, $C = {}^{31}P$, 100% natural abundance), and a full



(I)

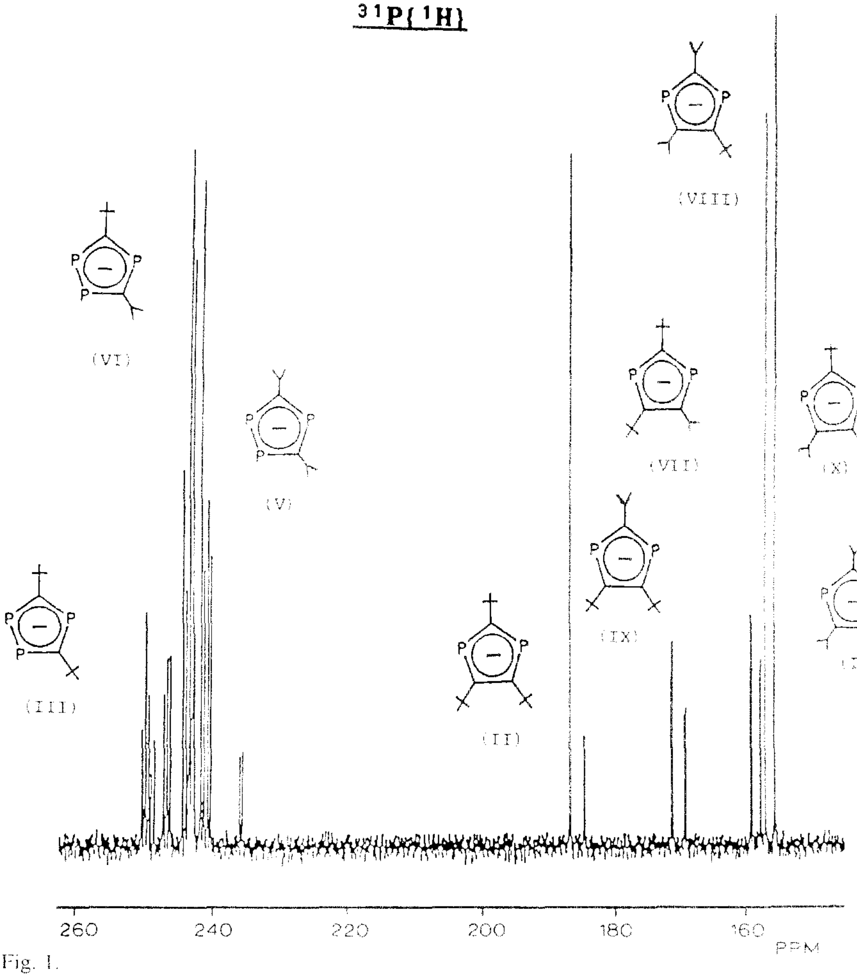


Fig. 1.

analysis of VI has been carried out *. It is interesting to note that the cross ring coupling constant $^2J(PP)$ can be measured in a diphosphollide for the first time. Confirmation of the existence in solution of all nine possible di- and tri-phosphollide ion species comes from mass spectroscopic analysis of the mixture of the green ferrocene-like complexes XI–XVI, which are obtained by treatment of the mixture of di- and tri-phosphollide ions with $FeCl_2$, and which contain mixtures of the $P_3C_2{}^tBu_2$, $P_2C_3{}^tBu_3$, $P_3C_2{}^iPr_2$, $P_2C_3{}^iPr_3$, $P_3C_2{}^tBu{}^iPr$, $P_2C_3{}^tBu_2{}^iPr$, and $P_2C_3{}^tBu{}^iPr_2$ rings.

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* II: δ(P) 186.9 (In ppm rel. H_3PO_4). III: δ(P(1)) 243.1, δ(P(2)) 249.7; ^2J(P(1)P(2)) 47.6 Hz. IV: δ(P) 155.0. V: δ(P(1)) 241.4, δ(P(2)) 246.6; ^2J(P(1)P(2)) 47.9 Hz. VI: δ(P(1)) 254.2, δ(P(2)) 238.5, δ(P(3)) 242.7; ^1J(P(1)P(2)) 457.2 Hz, ^2J(P(1)P(3)) 47.5 Hz, ^2J(P(2)P(3)) 35.0 Hz. VII: δ(P(1)) 171.1, δ(P(2)) 169.0; ^2J(P(1)P(2)) 27.4 Hz. VIII: δ(P(1)) 158.7, δ(P(2)) 157.3; ^2J(P(1)P(2)) 16.5 Hz. IX: δ(P) 184.5. X: δ(P) 156.5.

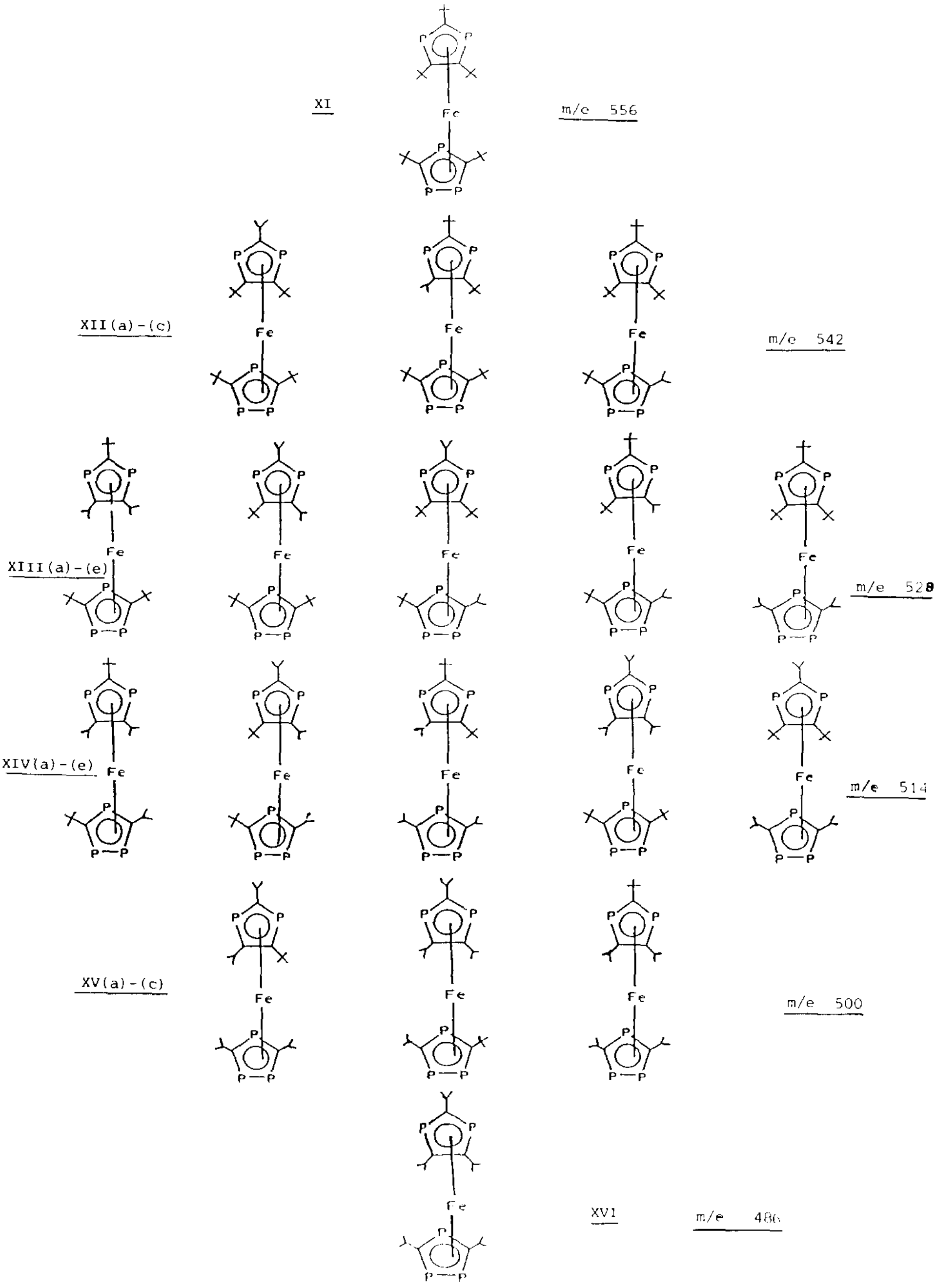

Fig. 2.

The mass spectrum of the products reveals parent ion peaks at *m/e* 556, 542, 528, 514, 500 and 486 which can be readily assigned to the complexes XI–XVI shown in Fig. 2. The variation in intensities of the parent ion peaks in the spectrum is noteworthy, reflecting the number of possible isomers that can exist for each individual sandwich compound. Interestingly, the 18 pentaphospha-ferrocene complexes containing mixtures of di- and tri-phosphacyclopentadienyl ring systems predominate, rather than any of the possible hexaphospha-ferrocenes. This presumably results from the sterically favourable miss-match of the organic substituents in each ring in the former complexes. Surprisingly, the parent ion peak for the known [Fe($P_3C_2{}^tBu_2$)$_2$], [1], is not seen in the mass spectrum of the mixture, and the peak of the new corresponding hexaphosphatetraisopropyl derivative [Fe(η^5-$P_3C_2{}^iPr_2$)$_2$] is extremely weak. Likewise, no evidence was found for any iron complexes containing two η^5-$P_2C_3R_3$ or η^5-$P_2C_3R_2R'$ ring systems (R,R′ = ^{t}Bu, ^{i}Pr).

The mechanism of this unusual ring formation reaction is currently under study, as is the possibility of incorporating other heteroatoms into these types of ring systems and, *inter alia*, their metallocene analogues.

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