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P_7R_3 , Cs_3P_{11} and Cs_4P_{14}

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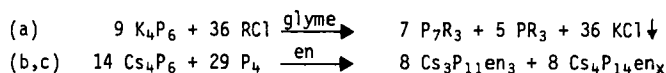
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Alkali Metal Hexaphosphenes(4) as Sources for the Polycyclic Compounds P_7R_3 , Cs_3P_{11} and Cs_4P_{14}

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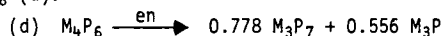
The alkali metal hexaphosphenes(4) M_4P_6 ($M=K, Rb, Cs$) are built up in the solid state by cations M^+ and a monocyclic six membered planar ring P_6^{4-} /1,2/. Reactions with RCl ($R=SnMe_3$) in glyme at $-70^\circ C$ led to the well known heptaphosphanortri-cyclenes P_7R_3 (a), and with P_4 in en to the undecaphosphide anion P_{11}^{3-} in form of the solvated crystalline Cs compound (b) as well as to a quadrodecaphosphide (c) P_{14}^{4-} , known already from a sodium compound.



The ^{31}P NMR spectra of the purple solutions of the compounds M_4P_6 in en yield at $+10^\circ C$ three singulets:

comp.	$\delta(P_6^{4-})$	$\delta(P_7^{3-})$	$\delta(P^{3-})$
K_4P_6	+ 473	- 123	- 270
Rb_4P_6	+ 337	- 121	- 266
Cs_4P_6	+ 349	- 115	- 256

The temperature and time dependent spectra are in agreement with the disproportion of M_4P_6 (d):



The low field signals we ascribe either to a valence fluctuating unit P_6^{4-} with one delocalized double bond or to an aromatic 2π (10π) system with 34 electrons. Up to now addition reactions at the double bond failed. The high field signals around $\delta=-120$ are due to the valence fluctuating anion P_7^{3-} , whereas the signals around $\delta=-260$ originate from the solved M_3P compounds. The insoluble dispersed compounds in glyme ($-70^\circ C$) yield only a poorly resolved ^{31}P NMR multi-plett in the low field region (K_4P_6 : + 90 to + 280; Rb_4P_6 : + 120 to + 300; Cs_4P_6 : + 150 to + 350), which in general is in agreement with the electron deficient compounds.

/1/ W.Schmettow, A. Lipka, H.G. v.Schnering, Angew.Chem. 86(1974)379; Angew.Chem. Int.Ed.Engl. 13(1974)5

/2/ H.-P.Abicht, W. Hönle, H.G. v.Schnering, Z.Anorg.Allg.Chem. 519(1984)7