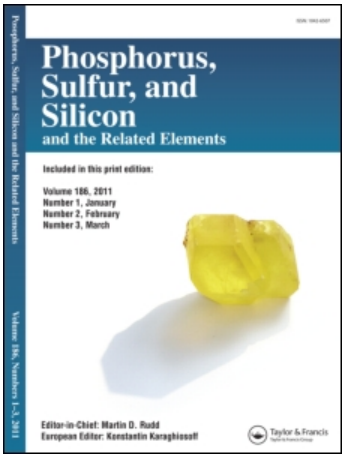

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Alkali Metal Hexaphosphenes(4) as Sources for the Polycyclic Compounds P_7R_3, Cs_3P_{11} and Cs_4P_{14}

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The alkalimetal 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°C led to the well known heptaphosphanortricyclenes 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.

(a) $9\ K_4P_6 + 36\ RCl \xrightarrow{glyme} 7\ P_7R_3 + 5\ PR_3 + 36\ KCl\downarrow$

(b,c) $14\ Cs_4P_6 + 29\ P_4 \xrightarrow{en} 8\ Cs_3P_{11}en_3 + 8\ Cs_4P_{14}en_x$

The ^{31}P NMR spectra of the purple solutions of the compounds M_4P_6 in en yield at +10°C three singuletts:

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	+ 348	- 115	- 256

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

(d) $M_4P_6 \xrightarrow{en} 0.778\ M_3P_7 + 0.556\ M_3P$

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 δ=-120 are due to the valence fluctuating anion P_7^{3-}, whereas the signals around δ=-260 originate from the solved M_3P compounds. The insoluble dispersed compounds in glyme (-70°C) yield only a poorly resolved ^{31}P NMR multiplett 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.

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