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Molecular Structure of Phosphinidene Phosphates

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Molecular Structure of Phosphinidene Phosphates

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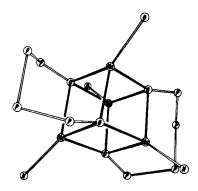
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Alkalimetal diphenylphosphinites degrade (Ph-P)₅ and P₄ to give anions containing a chain of 2, 3 or 4 four- and two-coordinated phosphorus atoms. Representatives of the chain with two four-coordinated and one two-coordinated P atoms became first available from the aminolysis of tris(phosphoryl)phosphides¹.

The products might be understood as phosphoryl-phosphides with an anionic charge concentrated at the two-coordinated P atom corresponding with the easy addition of two $M(CO)_5$ groups 1 . X-ray structure analyses show however the cations to be primarily (in the case of $R'_2NH_2^+$) or exclusively (in the case of alkalimetal cations) coordinated to the oxygen of the phosphoryl unit; P-P as well as P-O bond lengths are in accordance with the phosphinidene-phosphate formulae shown.

Anions with two phosphoryl ends chelate the alkalimetal cation, whereas, in the case of $R'_2NH_2^{-1}$ there is only a weak interaction between anion and cation. The coordination of the alkalimetal ion is completed by dimerization and by addition of acetonitrile and tetrahydrofurane. For $Na_2P_2(Ph_2P0)_2$ a rather perfect Na_4O_4 cubane skeleton is formed with an unusual coordination.



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