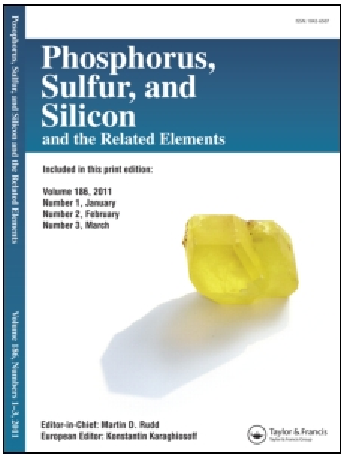

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Anionic Phosphinomethanides as Building Blocks for Heterocycles Containing Elements of Group 2 and 12

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Anionic phosphinomethanides are very soft donors to coordination centers. Though at least the light earth alkaline metals are extremely hard acceptors and therefore normally do not form stable complexes with e.g. phosphine ligands, various complexes of Be, Mg, Ca or Sr with one or more metal to phosphorus bonds can be obtained with this type of anionic ligands. The complexes obtained possess a spirocyclic or tricyclic backbone, depending on the nature of the phosphinomethanide and the metal. Diphosphinomethanides even form complexes with Be and Mg, where no other metal to ligand contacts are observed than metal-phosphorus bonds. In addition, also the metals of the zinc triad are included in the investigation. Most noteworthy, beryllium and zinc complexes with a given phosphinomethanide ligand turn out to be essentially isostructural, despite their highly different radii, which is explained by the covalent contribution to the bonding in these complexes.

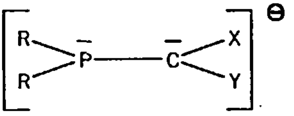
Keywords: Phosphinomethanides; earth alkaline metals; zinc triad; spirocycles; tricycles

Carbon and particularly phosphorus in anionic phosphinomethanides are very soft donors. It therefore was open to question, whether a strategy was conceivable to combine these ambident systems even with a group of elements which contain the hardest acceptors: the alkaline earth metals. Whereas phosphine complexes of the earth alkaline metals are essentially unknown, phosphanides successfully have been employed to create M-P bonds with these metals. Phosphinomethanides are much more alike phosphines in the sense, that in both cases, phosphorus is tri-coordinate and uncharged, in contrast to phosphanides, where it is two-coordinate and the negative charge is centered directly on the phosphorus atom.

The concept of introducing phosphinomethanides as ligands to earth alkaline metal centers would not only allow for the isolation and characterization of ring- and multiple-ring systems (multi-spirocyclic compounds) with these elements, but also give deep insight into the nature of more or less covalently bonded, hydrocarbon soluble derivatives of the alkaline earth metals. In order to get a more profound understanding of the nature of these systems, also elements of the zinc group were included in this study.

In fact, we succeeded in the isolation of various heterocycles containing beryllium, magnesium, calcium and strontium together with carbon and

Mono-and *di*-phosphinomethanides $[(R_2P)C(X)(Y)]^{\ominus}$ (*I*) and $[(R_2P)_2C(X)]^{\ominus}$ (*II*), respectively, are anionic, ambident ligands with remarkable properties: In these very soft ligands, phosphorus and carbon possess the same valence electron count and coordination number and both are linked together directly. Thus the reactivity of these two elements, which are linked in the periodic table via a diagonal relationship, towards nucleophiles may be compared. In fact, by tuning the properties of these nucleophiles in choosing the appropriate substituents (R, X, Y), an electrophile E may form E-C, E-P or both types of bonds simultaneously [1].



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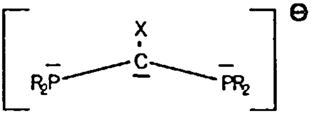
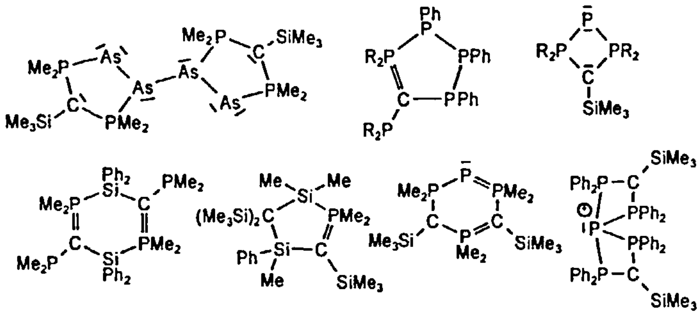
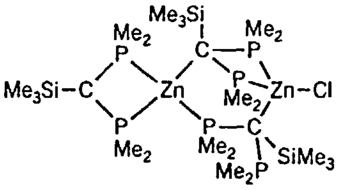


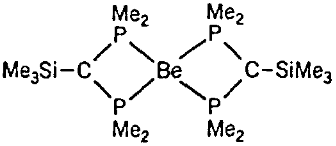
II

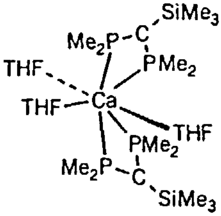
In consequence, these species have been used in our group to synthesize various novel heterocycles incorporating main group [1-3], transition [4] and even lanthanide [5] elements in carbon and phosphorus containing ring systems. Selected heterocycles obtained from the reaction of main group element halides with lithium phosphinomethanides are given below [2].

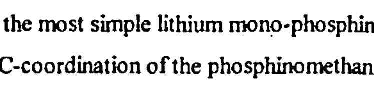


phosphorus as ring members. In some cases, spirocycles also containing lithium were obtained. A subtle balance of coulomb interactions and covalent bond contributions controls the specific arrangement of the phosphinomethanide donor to the metal acceptors and hence its orientation (sequence of the ring atoms). In dinuclear systems, also tricyclic arrangements are observed. Some examples of the complexes obtained are given below [3].



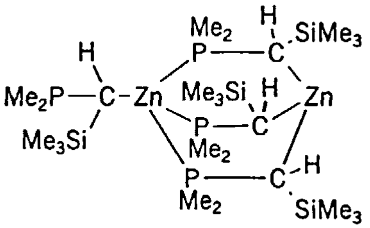


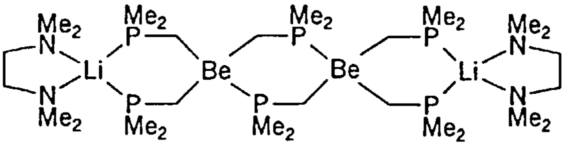




With the most simple lithium mono-phosphinomethanide Li[CH_2PMe_2], only C-coordination of the phosphinomethanide to the metal is observed in the case of magnesium. With the lithium di-phosphinomethanide Li[$C(PMe_2)_2SiMe_3$], in most cases high phosphine coordination numbers of the metals are achieved, e.g. in Be[$C(PMe_2)_2SiMe_3$]$_2$, beryllium gains the coordination number four by forming four metal-phosphorus bonds and in the anionic metalate Mg[$C(PMe_2)_2SiMe_3$]$_3^{\ominus}$, magnesium forms even six metal-phosphorus bonds. The di-phosphinomethanide $[C(PMe_2)_2SiMe_3]^{\ominus}$ in most cases acts as a P,P-chelate ligand, but in the zinc derivative $Zn_2[C(PMe_2)_2SiMe_3]_3Cl$, three different coordination modes of the same ligand are observed.

The most noteworthy result is the fact, that beryllium and zinc derivatives show a high degree of similarity in their structural behavior, even in rather complex arrangements. This similarity has not been documented before and is a consequence of the similarity in the covalent bond character of these two elements - the (highly different) ionic radii obviously do not display any significant influence. Two examples of heterocycles of beryllium and zinc are shown below, each possessing the respective zinc/beryllium isostructural counterpart.





In the zinc compound (as well as in the beryllium analogue), the two metals adopt different coordination numbers: one of the zinc atoms has coordination number three, the other one coordination number four.

The spirocyclic beryllium derivative of the "simple" mono-phosphinomethanide $[CH_2PMe_2]^{\ominus}$ (as well as the zinc analogue), in contrast to the magnesium case discussed above, exhibits metal-phosphorus bonds. This observation, which is in contrast to the expectation from simple metal seize considerations, again obviously is a consequence of an enhanced covalent bond contribution in the beryllium compound, compared to the magnesium case. In fact, the very soft phosphinomethanide ligands seem to are a versatile tool to study subtle differences in the bonding properties of hard metal centers, which cannot be evaluated with "normal", hard donor ligands (O- or N- donors) preferentially used as ligands for this type of metal centers.

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