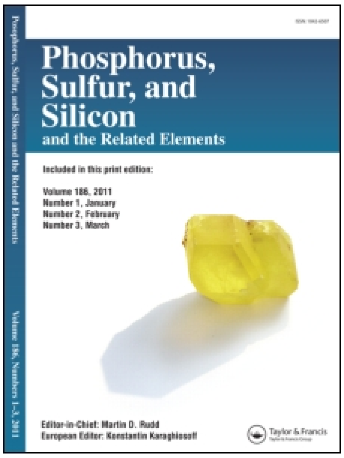

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Functional Phosphinomethyl Derivatives: Some Parallels Between Organophosphorus and Carbon Chemistry

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FUNCTIONAL PHOSPHINOMETHYL DERIVATIVES: SOME PARALLELS BETWEEN ORGANOPHOSPHORUS AND CARBON CHEMISTRY

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Abstract The reactivity of P and C in saturated and unsaturated C-P linked organophosphorus species is compared. Novel type main group element phosphine complexes and 1.3 diphospha-allyl, -allene and -butadiene compounds are obtained and characterized by NMR spectroscopy and X-ray diffraction analysis.

INTRODUCTION

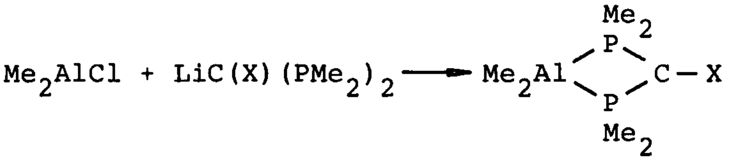
From the diagonal relationship between carbon and phosphorus, some similarities may be expected. Indeed, it has been shown, that P-P and C-C linkages show some analogies. Both elements may form chains, rings and cages. The reactivity of phosphorus and carbon in σ^3-P-C linked compounds is comparable, if both elements exist in an isoelectronic state, as in phosphinomethanides I

$$\underset{\text{I}}{[R_2P\text{-}CR'_2]^{\ominus}} \qquad (R = \text{organic group};\ R' = H,\ PR_2,\ SiMe_3)$$

In I both phosphorus and carbon are susceptable to electrophilic attack. Consequently with metals as the electrophile, either P or C coordination, or both, takes place. This may be controlled by the choice of groups R and R' and the reaction conditions.

NOVEL TYPE MAIN GROUP PHOSPHINE COMPLEXES

Whereas monophosphinomethanides react with aluminum chlorides to give dimeric, six membered ring compounds, diphosphinomethanides give phosphine complexes with tetra- or hexacoordinated aluminum (1, 2). Compound 2 (X = $SiMe_3$) shows a distorted octahedral AlP_6 coordination with planar carbanions.



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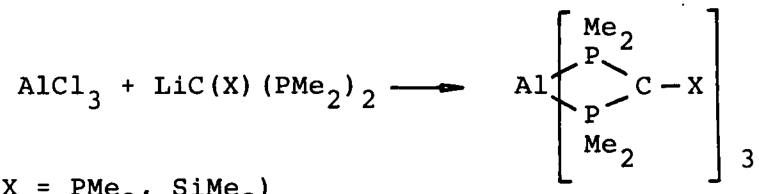
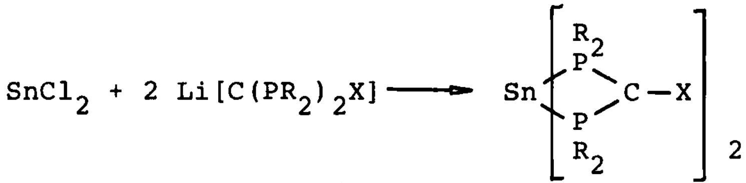


2

(X = PMe_2, $SiMe_3$)

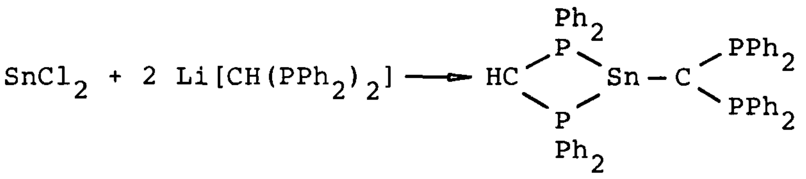
Sn(II) forms stable, monomeric, ψ-trigonal bipyramidal complexes 3-5 with phosphinomethanide ligands.



3: R = Me, X = PMe_2; 4: R = Me, X = $SiMe_3$
5: R = Ph, X = PPh_2

The lone pair at Sn occupies an equatorial position. The four membered chelate rings, in contrast to the aluminum case, are bent away from this lone pair.

In contrast to this, in 6 the Sn(II) metal center displays tricoordination.

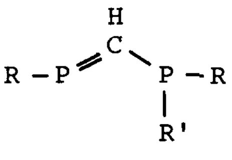


6

similar complexes of germanium and lead have also been obtained. Most interestingly, lanthanoides show π-allylic type of coordination, e.g. in $La(Ph_2PCHPPh_2)_3$. From these observations, we conclude, that C and P reactivity in phosphinomethanides indeed is comparable. Novel coordination compounds may be obtained, where C and P rival for the metal center and therefore, dynamic processes are quite common.

DIPHOSPHA ANALOGUES TO ALLENE AND ALLYLIC COMPOUNDS

Another type of analogy between phosphorus and carbon is found in unsaturated systems, e.g. in the series C=C, C≡C, M=C/P=C, P≡C, P=P, M=P and related linkages. Some new examples for this analogy are provided by 1.3-diphosphapropenes 7 as starting materials, which formally are related to diphosphinomethanides 8 by the loss of a carbanionic substituent R'.



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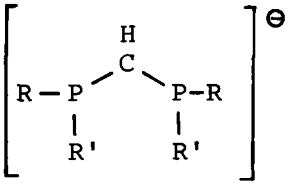
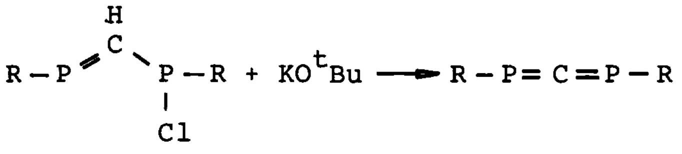


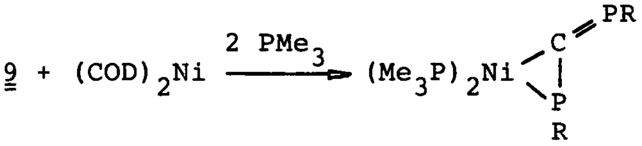
8

From 7 (R = 2.4.6-$^{t}Bu_3C_6H_2$, R' = Cl: 7a) the allene analogue 9 may be obtained. 9 is fluxional in solution due to a rotation around the $P\text{-}C_{(R)}$ single bond. It may be resolved, the enantiomeres are stable at +25°C for several days.



7 9

Obviously, no rotation around the P=C double bond occurs. 9, an analogue to CS_2, is an excellent ligand, e.g. 10 is formed with Ni(0).

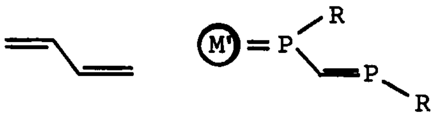


10

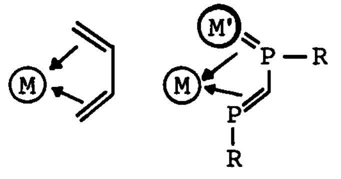
10 again is fluxional in solution, at +25°C, the PR groups equilibrate.

Both nucleophiles and electrophiles attack 9 at phosphorus. Thus, Me_3PCH_2 reacts with 9 to give $R\text{-}P\text{=}CH\text{-}P(R)\text{-}CH\text{=}PMe_3$, a compound, where σ^2-, σ^3- and σ^4-P-atoms are linked together via methine bridges.

Substitution reactions at 7a proceed via a novel "phospha S_N2' allyl rearrangement" route. A stable diphosphaallyl anion was isolated from R-P=CH-P(R)H and ^{t}BuLi, but the respective cationic species could not be obtained in a free state. However, it may be stabilized as a ligand in transition metal complexes. Thus, from 7a and $Na[M(CO)_3Cp]$, s-trans heterobutadiene species (1) are isolable, which show a butadiene-like coordination behavior to complex metal fragments (2) (Ⓜ = $Fe(CO)_3$; M' = $Cp(CO)_2M$; M = Mo, W).



(1)



(2)