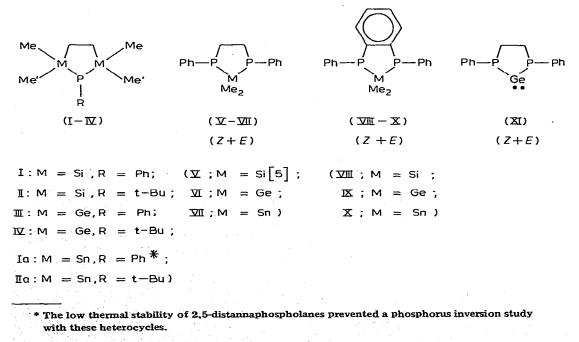# INVERSION AT PHOSPHORUS IN DIMETALLA-IVB-PHOSPHOLANES AND METALLA-IVB-DIPHOSPHOLANES

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Summary

Inversion at phosphorus in dimetalla-IVB-phospholanes, metalla-IVB-diphospholanes and in a diphosphanylgermylene has been studied by ^{1}H and ^{31}P dynamic NMR spectroscopy.

We have recently described the synthesis of a new series of sila-, germa- and stannaphospholanes of various structures such as 2-metallaphospholanes [1], 2,5-dimetallaphospholanes and 2-metalla-1,3-diphospholanes [2]. We showed,

(I—IV)	(V—VII)	(VIII—X)	(XI)
	(Z + E)	(Z + E)	(Z + E)

I : M = Si , R = Ph;   (V ; M = Si [5] ;   (VIII ; M = Si ;

II : M = Si , R = t—Bu ;   VI ; M = Ge ;   IX ; M = Ge ;

III : M = Ge, R = Ph;   VII ; M = Sn)   X ; M = Sn)

IV : M = Ge, R = t—Bu ;

Ia : M = Sn, R = Ph * ;

IIa : M = Sn, R = t—Bu)

* The low thermal stability of 2,5-distannaphospholanes prevented a phosphorus inversion study with these heterocycles.

TABLE 1

INVERSION BARRIERS OF COMPOUNDS I—XI CALCULATED FROM THE EYRING EQUATION

Compound	t_c (°C) [a]	K_c (s^{-1}) [b]	$\Delta G_c^{\star}$ (kcal/mol)
I	−17	58	12.8
II	−57	20	11.2
III	78	270	18.3
IV	57	80	16.5
V	123	400	18.6
VI	195	910	21.4
VII	169	1510	19.0
VIII	113	370	18.2
IX	175	630	20.8
X	125	780	18.2
XI	145	963	19.0

[a] t_c = coalescence temperature. [b] K_c = rate constant at temperature t_c.

with a series of 2-dimethylmetalla-1-phenylphospholanes [3], that the pyramidal inversion barrier at phosphorus increased with the electronegativity of the neighbouring metal, in agreement with the observations by Mislow et al. on open-chain metallaphosphines [4]. We have now confirmed the generality of this phenomenon for a series of 2,5-dimetallaphospholanes and 2-metalla-1,3-diphospholanes. The special case of diphosphanylgermylene has also been studied.

With 2,5-dimetallaphospholanes, the ^{1}H dynamic NMR study involved determination of the coalescence of diastereotopic methyls bonded to the metal [2]. With 2-metalla-1,3-diphospholanes, the coalescence of respective signals of Z and E diastereoisomers was determined by ^{31}P NMR spectrocopy.

A line-shape analysis, using Saunders' program [6] and matrix method of Kubo [7] and Sack [8], was used to simulate spectra at various rates of exchange. Substitution of rate constants and temperatures at coalescence into the Eyring equation gave the values of the inversion barrier (Table 1).

Variable temperature studies were performed in toluene-d_8 (compounds I—IV), tetraline (V—X) and benzonitrile (XI).

The results confirm the significant role of electronegativity [9] of metal atoms bonded to phosphorus on the height of pyramidal inversion barrier in metalla-IVB-phosphines; the value of $\Delta G^{\star}$ increases in the order Si (1.90) < Sn (1.96) < Ge (2.01).

Of particular interest is the observation that the coalescence temperature of the two diastereoisomers of the diphosphanylgermylene (XI) is 50°C lower than in the corresponding heterocycle with tetracoordinated germanium (VI). This lowering of the energy barrier (2.4 kcal/mol) can be associated to the presence of bivalent germanium and delocalization of the phosphorus lone pairs into a vacant p orbital of the sp_2 hybridized germanium atom.

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