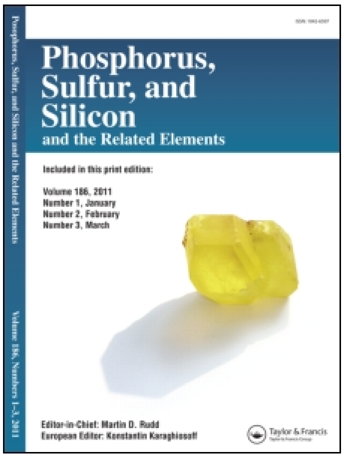

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Wilfried Becker[a]; Dietmar Schomburg[b]; Peter G. Jones[a]; Reinhard Schmutzler[b]
[a] Institut für Anorganische und Analytische Chemie der Tehnischen Universität, Hagenring 30, Braunschweig, F.R.G. [b] Gesellschaft für Biotechnologische Forschung m.b.H., Mascheroder Weg 1, Braunschweig, F.R.G.

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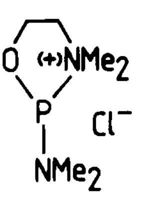
PROPERTIES AND REACTIONS OF 3-AZA-1-AZONIA-1,1,3-TRIMETHYL-2λ^3-PHOSPHOLIDINES (INTRAMOLECULARLY STABILIZED PHOSPHENIUM CATIONS)

WILFRIED BECKER[a], DIETMAR SCHOMBURG[b], PETER G. JONES[a]
AND REINHARD SCHMUTZLER[a]

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, D-3300 Braunschweig, F.R.G.[a] — *Gesellschaft für Biotechnologische Forschung m.b.H., Mascheroder Weg 1, D-3300 Braunschweig, F.R.G.*[b]

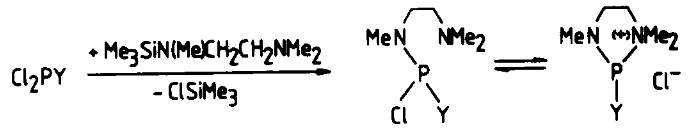


1

In contrast to the well-known phosphorus(III) donor systems, comparatively few cases are known in which P(III) displays acceptor properties, cf., e.g. [1,2]. Adducts of the type $X_3P \leftarrow Nu$ (Nu = nucleophile) are of special interest as models of nucleophilic substitution reactions at P(III), and have been isolated, in some cases[3]. Compound **1**, reported in 1966[4], probably constitutes the first case of an intramolecular complex involving P(III) as acceptor.

1. Compounds with λ^3phosphorus(III).

The covalent compounds **2** - **6** and the ionic compounds **7** - **10** were obtained, in accord with eq. (1) (see also ref.[5]).



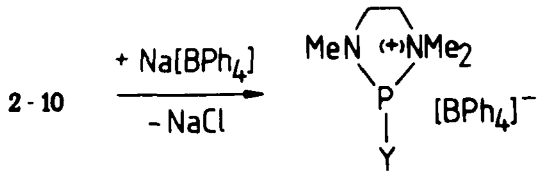
(1)

Y = Me, **2**; Ph, **3**; Bu^t, **4**; CCl_3, **5**; CF_3, **6**;

Y = Cl, **7**; OMe, **8**; OPh, **9**; NEt_2, **10**.

The tetrachloroaluminates, $[Me_2NCH_2CH_2N(Me)P(Me)]^+$ $[AlCl_4]^-$, **11**, and $[Me_2NCH_2CH_2N(Me)P(Ph)]^+$ $[AlCl_4]^-$, **12**, were formed in the reactions of **2** and **3**, respectively, with $AlCl_3$[6]. Reaction of $Me_2NCH_2CH_2N(Me)SiMe_3$ with $PhPF_2$, with elimination of Me_3SiF, led to the formation of $Me_2NCH_2CH_2N(Me)P(Ph)F$, **13**, (similarly to eq. (1)). Upon reaction of **13** with F_3B-OEt_2, coordination of

BF_3 at the Me_2N nitrogen (formation of $Me_2N(BF_3)CH_2CH_2N(Me)P(Ph)F$, **14**) was observed, while the expected tetraphenylborate, $[Me_2NCH_2CH_2N(Me)P(Ph)]^+ [BPh_4]^-$, was not formed. In general, the equilibrium described in eq. (1) can be shifted from the molecular species to their intramolecularly coordinated isomers, **15**-**22**, by reaction of **2**-**10** with $Na[BPh_4]$ (eq. (2))[7]; this amounts to the exchange of Cl^- for a non-coordinating anion.



(2)

Y = Me, **15**; Ph, **16**;
Bu^t, **17**; CCl_3, **18**,
Cl, **19**; OMe, **20**;
OPh, **21**; NEt_2, **22**.

The identity of **16** as an intramolecular complex was confirmed by a single crystal X-ray diffraction study. A nearly planar nitrogen atom was observed in the $CH_2(Me)NP$ grouping; r ($CH_2(Me)N$–P) 166 pm; r (Me_2N–P) 188 pm[7].

Variable temperature ^1H n.m.r. spectra

From the variable temperature ^1H n.m.r. spectra of some ionic compounds of the type $[Me_2NCH_2CH_2N(Me)P(Y)]^+ X^-$ (Y = OMe, OPh, Me, Ph; X = Cl, $[BPh_4]$), $\Delta G^{\ddagger}$ values for the positional exchange of the two diastereotopic methyl groups at the donor nitrogen atom could be estimated. Depending on the substituent Y at phosphorus, inversion at nitrogen and free rotation about the Me_2N–CH_2 bond were restricted as a result of the coordination, and ^1H n.m.r. spectra, as for **15** (Fig. 1) were observed.

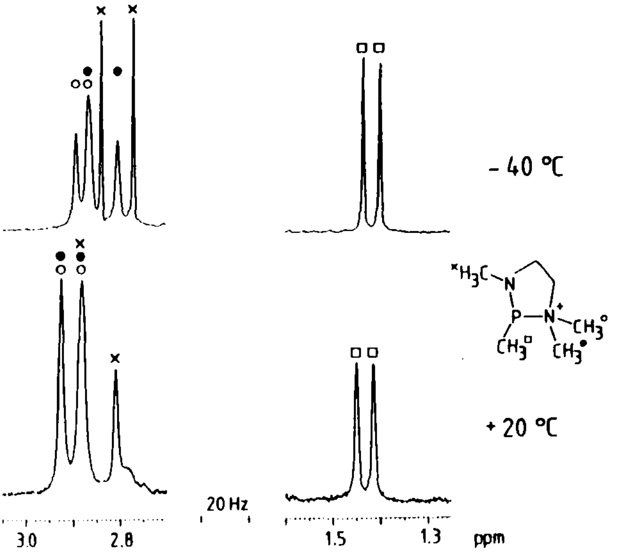


Fig. 1: ^1H n.m.r. spectra of $[Me_2\overline{NCH_2CH_2N(Me)P}(Me)]^+ [BPh_4]^-$, **15** at +20 °C and -40 °C.

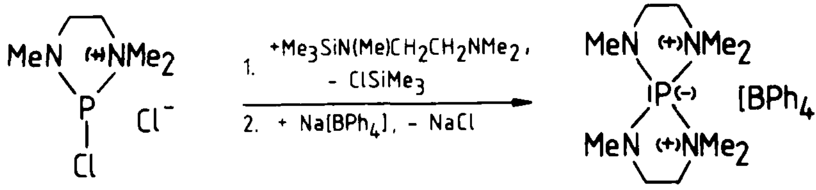
$\Delta G^{\ddagger}$ values (in kJ/mol) were determined, using the Eyring equation[8]. They suggest the following order of increasing stability of the donor-acceptor bond, depending on Y and X for compounds of type $[Me_2\overline{NCH_2CH_2N(Me)P}(Y)]^+ X^-$:

Y = **Ph** (52.0), **Me** (55.3) < **OMe** (59.7) < **Bu^t** (>59), **OPh** (>60), **CCl$_3$** (>60);

X = **Cl** << **BPh$_4$** (Difference for any substituent Y > 10).

2. Substitution reactions

Substitution of Cl in **7** by $Me_2NCH_2CH_2N(Me)$ and exchange of Cl^- for BPh_4^-, in accord with eq. (3) furnished compound **23**, involving hypervalent phosphorus[6] (δ_P +154; $^3J(HP) = 7.8$ and 3.8 Hz for the $NC\underline{H}_3$ and $N(C\underline{H}_3)_2$ groups).



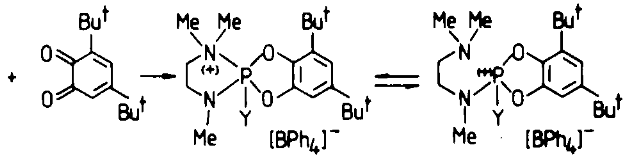
(3)

7 **23**

3. Compounds involving phosphorane or phosphonium structures

From compounds **15** - **17** the P(V) compounds, **24** - **26**, were obtained by reaction with 3,5-di-tert-butyl-o-benzoquinone.

15, 16, 17



(4)

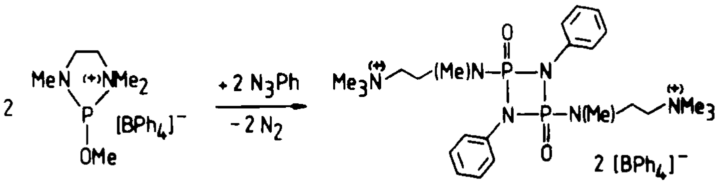
24, Y = Me;
25, Y = Ph;

26, Y = Bu^t.

The variable temperature ^{1}H n.m.r. spectra of **25** indicated the presence of two diastereomers at low temperature. Above room temperature these diastereomers are interconverted, within the time scale of the n.m.r. experiment, possibly via a Berry pseudorotation mechanism^9. At 55 °C two signals for the $C(C\underline{H}_3)_3$ protons, corresponding to one diastereomer, were observed while at -20 °C four signals for the $C(C\underline{H}_3)_3$ protons, as expected for two diastereomers, were seen.

4. Staudinger reaction

The reaction of **10** with phenyl azide and subsequent exchange of Cl$^-$ for [BPh$_4$]$^-$ gave the expected compound, $[\mathrm{Me_2\overline{NCH_2CH_2N(Me)P}(NEt_2)}]^+$ [BPh$_4$]$^-$, **27**. Compound **20**, however, furnished the structurally rearranged dimer, **28**.



(5)

20 **28**

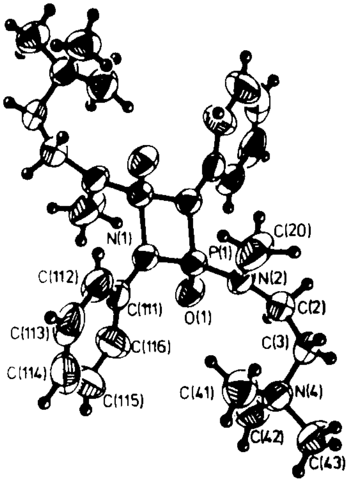
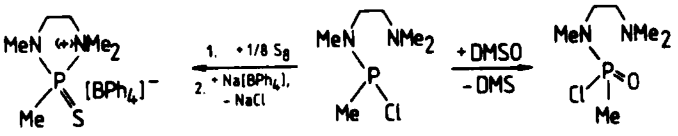


Fig. 2: Crystal structure of the di-cation of **28**

5. Oxidation with sulfur and dimethyl sulfoxide (DMSO)

The phosphoryl and thiophosphoryl derivatives **29** and $[\mathrm{Me_2\overline{NCH_2CH_2N(Me)P}(:S)Me}]^+\ Cl^-$, **30**, were formed in the reaction of **2** with DMSO and S_8, respectively. When compound **30** was treated with $Na[BPh_4]$, the tetraphenylborate, **31**, was formed.



31 **2** **29**

(6)

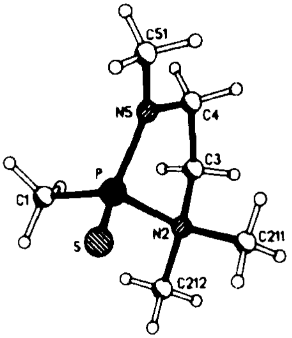


Fig. 3: Crystal structure of the cation of **31**

Acknowledgements

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