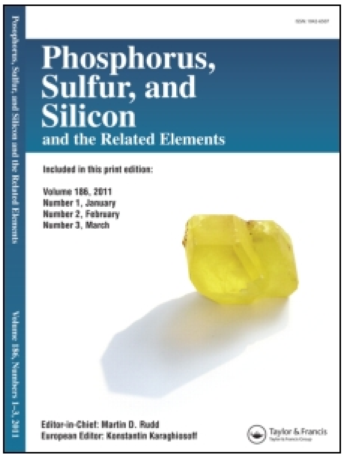

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Bis-and Trismethylenephosphorane. Experimental and Theoretical Evaluation of Bonding Properties

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BIS- AND TRISMETHYLENEPHOSPHORANE. EXPERIMENTAL AND THEORETICAL EVALUATION OF BONDING PROPERTIES.

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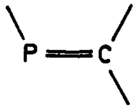
Abstract. The electronic properties of the title compounds are evaluated by electrochemical and quantum chemical investigations.

Within recent years considerable effort has been drawn to the syntheses and structural elucidations of methylenephosphanes[1], **1**, bismethylenephosphoranes[2], **2**, and the trismethylenephosphorane anion[3], **3**. Therefore we have carried out electrochemical investigations via cyclic voltammetry on **1** to **3**, supplemented by quantum chemical investigations at a semiempirical and ab initio double-ζ level. For the measurements a special low temperature cell was constructed which allows easy handling of the very air sensitive P(III)-double bond systems.



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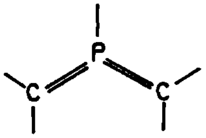

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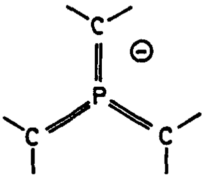


3

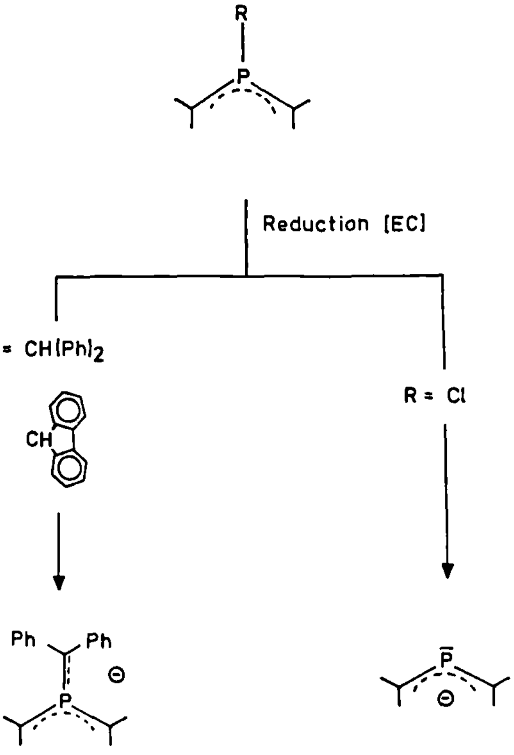
1. Methylenephosphanes

As predicted by theory[4a] they possess two closely spaced frontier orbitals[4b], $\sigma(P)$ and $\pi(PC)$. The double bond is essentially unpolar[5]. Hence for parent **1** a normal electron demand with respect to a [4+2]-cycloaddition is to be expected. Cyclic voltammograms on a selected variety of methylenephosphanes and of iminophosphanes reveal at times one irreversible reduction peak and one irreversible oxidation peak. On the contrary, the diaminodiphosphine (NR_2, $R=SiMe_3$) undergoes reversible anion radical formation but the cation formation is still irreversible. The trends in the substituent effects on the methylenephosphanes are as follows [in butyronitrile, -100 °C, in references to the standard calomel electrode (SCE)]: (a) but^t-P=CH-but^t, 2.41 V [$E_p^{ox,a}$ (anodic)], -2.67 V [$E_p^{red,c}$ (cathodic)]. (b) $SiMe_3$ groups at carbon considerably lower the oxidation as well as the reduction potentials for **1**. The lowest reduction potential possesses $ClP=C(SiMe_3)_2$, -1.70 V [$E_p^{red,c}$], 2.94 V [$E_p^{ox,a}$]. On the basis of the peak potentials one can assign experimentally the substituent effects exerted on the frontier orbital energies of parent methylenephosphane.

2. Bismethylene- and Trismethylenephosphorane

They adopt a planar structure despite a weak Jahn-Teller force acting for pyramidalization at phosphorus[6]. The π-system is described as an ylid rather than as an ylen since the d-orbital participation in bonding at phosphorus is negligible. Similar conclusions hold for **3**. Quantum chemical investigations reveal the following aspects: (a) π-electron accepting substituents (e.g. silyl) stabilize the π-system in **2** and **3**, π-electron donating groups (e.g. amino) do the opposite. (b) Accordingly, a triplet ground state over a singlet ground state comes to the fore with increased substitution of **2** or **3** by π-donating substituents at the carbon atoms. (c) The energy lowest triplet state is strongly pyramidalized at phosphorus. In the singlet state weak pyramidalization is only to be expected for unsymmetrical substitution at the carbons, i.e. at one carbon a π-donor and at the other carbon a (weak) π-acceptor. The electrochemical investigations on a selected variety of **2** (at each carbon atom two

SiMe$_3$ groups, R(at phosphorus)=Cl, NR$_2$, OR, alkyl) reveal similar trends for the reduction potentials, as compared with the methylenephosphanes. In most cases the waves for reduction or oxidation are irreversible. Only for R(at P)= CH=CHPh a reversible anion radical formation is observed. The lowest peak potentials for reduction are observed for R=Cl(at P) -1.85 V [$E_p^{red,c}$], while R=NR$_2$ possesses the highest reduction potential, -2.80 V [$E_p^{red,c}$]. The variation of R only slightly effects the peak potentials for oxidation. They range from 0.94 V [$E_p^{ox,a}$] (R=but^t) to 1.38 V (R=OPh). On the basis of the electrochemical measurements and in accordance with quantum chemical calculations one can assign a frontier orbital system comprised of a π-type allylic system occupied by four electrons. In addition the relative order of reduction and oxidation potentials for the various 2 allow an experimental assignment of the frontier orbital energies. In accordance with the experimental and theoretical findings on the bismethylenephosphoranes the ring closure reaction



is expected to occur conrotatory, in agreement with the experimental investigations[7]. Electrolysis of various derivatives of **2** opens two new synthetic routes, (a) to the trismethylenephosphorane anion system via hydrogen abstraction (**2**, e.g., R–$CHPh_2$) or alternatively with (b) Cl^- separation to the 2-phosphallyl system. Under the condition of low temperature cyclic voltammetry the latter is trapped with the solvent butyronitrile to the corresponding methylenephosphane. In the former case the trismethylenephosphorane anion undergoes reversible radical formation (stable at room temperature), e.g. R(at P)–CPh_2, R' (twice at each carbon)–$SiMe_3$, -0.32 V ($E_1{}^o$, 25 °C in butyronitrile, vs. SCE), while further oxidation leads irreversibly to the cation of **2**, 0.75 V [$E_p{}^{ox,a}$ 0.75 V].

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