μm^{-1}.[7] It should nevertheless be noted that the radiationless decay rate of S_2 (**1**, R = H), $k_{nr} \cong 2 \times 10^{11}\ s^{-1}$, calculated from $\phi_f = (5 \pm 1) \times 10^{-4}$ and $k_f \cong 1 \times 10^{8}\ s^{-1}$, is over 2 orders of magnitude larger than that predicted from an energy gap relation empirically parametrized for polyacenes.[51] Inasmuch as this correlation may be considered valid for the heterocycles **3**[4] and **1**, this discrepancy may be taken as an indication for the presence of an additional $n\pi^*$ state(s) between the $\pi\pi^*$ states S_1 and "S_2". Not surprisingly, the protonated forms of **1** exhibit normal S_1 fluorescence only, since the S_2–S_1 energy gap is further reduced upon protonation. E.g., a solution of **1**H^+ (R = Me) in 0.1 N aqueous sulfuric acid gave rise to a red emission (λ_{max} = 620 nm, $\phi_f = 5 \times 10^{-4}$) with a lifetime of $\tau_f = 0.6 \pm 0.1$ ns.

Another unusual feature is the near degeneracy of the lowest $\pi\pi^*$ singlet and triplet states of **1** (R = H), $|E(S_1) - E(T_1)| <$ 10 kJ/mol, and the short lifetime of the latter, $\tau(T_1, 300\ K) <$ 1 μs. The small singlet–triplet energy gap is a further manifestation of the frontier-orbital separation in space; a detailed discussion was given previously.[3] The short lifetime of T_1 is tentatively attributed to a rapid radiationless deactivation via $T_1 \rightarrow S_1$ intersystem crossing. Thus the unusual sequence of the excited-state energies of **1** (R = H), $E(S_2) >> E(S_1) \cong E(T_1)$, appears to result in a very rapid and efficient radiationless deactivation of this molecule after electronic excitation or triplet sensitization. As a consequence, **1** (R = H) is quite stable to photochemical decomposition.

Our tentative assignments of the ionization bands of compounds **1** (R = H and Me) as given in Table I are consistent with the previous assignments for **3** (a reassignment of the fourth π-band 1e″ is proposed, Figure 3)[33] and **4**[6] which were based on semiempirical and ab initio (STO-3G) calculations. However, we emphasize that both the previous calculations[6,33] and the present simple correlation procedure rely on the applicability of Koopmans' theorem. Such a procedure appears to be highly questionable in view of PPP CI calculations for **1** and **3** which predict that a simple one-to-one correspondence between ionization bands and canonical bonding orbitals does not exist for this type of compound.[30,31] Thus a more detailed investigation, including, e.g., the electronic absorption spectra of the corresponding radical cations, may well lead to a revision of some or all of the spectral assignments beyond bands 1 in this series of compounds.[52]

Acknowledgment. This work is part of Project 2.213-0.84 of the Swiss National Science Foundation. The picosecond laser studies were supported in part by the NSF. Financial support was received from Ciba-Geigy SA, Hoffmann-La Roche SA, Sandoz SA, and the Ciba-Stiftung. We are most grateful to Prof. F. Gerson and Dr. G. Plattner, Basel, for the ESR spectra of $1^{-\cdot}$ (R = H, Me), Prof. A. Zuberbühler, Basel, for the multiwavelength analysis[34] of the protonation equilibria, and Shell Chemical Co. for a generous gift of "Amine-RC-94".

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(52) A further pertinent paper dealing with the synthesis and spectroscopic properties of azacycl[3.3.3]azines has appeared after this manuscript was submitted: Rossman, M. A.; Leonard, N. J.; Urano, S.; LeBreton, P. R. *J. Am. Chem. Soc.* **1985**, *107*, 3884–3890.

Some Aspects of the Electronic Hypersurface of Bis(methylene)phosphorane. An Experimental and Theoretical Approach

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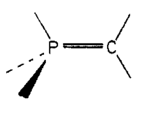
Abstract: Bis(methylene)phosphoranes possess a strongly polarized π-system, isoelectronic to the allyl anion. Jahn–Teller distortion of the electronic ground-state hypersurface causes weak pyramidalization at phosphorus. Its magnitude depends on the substituents. The electrocyclic ring-closure reaction to phosphacyclopropane is conrotatory. Electron-accepting substituents (e.g., silyl groups) at the carbon atoms stabilize the open bis(methylene)phosphorane and disfavor the ring-closure reaction. The electrochemical investigations are in support of the theoretical analysis. The redox reactions are irreversible. While the CV oxidation peaks are independent of the substituents on bis(methylene)phosphorane, the reduction peak potentials considerably increase with NR_2 or OR at phosphorus.

Coordination at phosphorus decreases in the order of structures **1**–**3**. From a historical point of view, the first member in this series, methylenephosphorane (**1**), has gained much attention, from experimental[1] as well as theoretical[2] investigators. In comparison, only recently the first synthesis and structural elucidation of



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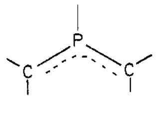

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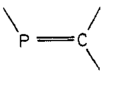

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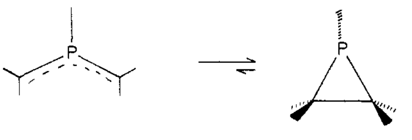
bis(methylene)phosphorane (**2**) have been reported.[3] To complete this palette a plethora of investigations has been reported on methylenephosphane (**3**).[4]

In the present publication we report for the first time on the physical properties of this new class of tricoordinated species, **2**. Its bonding will be compared with that in **1** and **3**. In addition, we relate our findings to electrochemical measurements on various substituted **2**. In detail we will consider the following aspects of **2**: (1) an analysis of bonding and the Jahn–Teller distortion of the ground-state hypersurface; (2) the electrocyclic reaction of **2** to the phosphacyclopropane system **2a**[5] (the latter finds its pendant in the chemistry of aziridines[6]; and (3) the electrochemical properties of **2**, which are obtained from studies with cyclic voltammetry.



2 2a

Theoretical Procedure

Our analysis of bonding is based on the results of MNDO[7] and ab initio SCF calculations. Geometry optimizations were performed with the Davidon–Fletcher–Powell method[8] utilizing the method of finite differences[9] for the evaluation of the gradients. For the ab initio calculations the following basis sets were used: (1) Basis I consists of Gaussian lobe functions.[10] It is of double-ζ quality, constructed from the following Huzinaga[11] bases: C, N, O, (7/3) in the contraction (4, 3 × 1/2, 1); P, (9/5) in the contraction (5, 4 × 1/3, 1); H, (3, 1). Polarization functions (p) for the hydrogens were added; $\zeta_p = 0.65$. (2) Basis II consists of basis I plus one set of polarization functions at all atoms. The d-exponents for the heavy atoms C, N, O, and P were chosen according to Ahlrichs et al.,[12] $\zeta_d(\mathrm{C}) = 0.30$, $\zeta_d(\mathrm{N}) = 0.95$, $\zeta_d(\mathrm{O}) = 1.25$, and $\zeta_d(\mathrm{P}) = 0.50$.

Experimental Section

Materials. Samples of the various bis(methylene)phosphoranes were kindly provided by Prof. Appel (University of Bonn). They were prepared according to the literature procedure.[3] In all electrochemical experiments butyronitrile was used as a solvent. Its purification was obtained according to the method of Van Duyne and Reilly.[13] Butyronitrile (Merck, for synthesis) was twice heated at 75 °C and stirred for several hours with a mixture of 7.7 g of Na_2CO_3 and 11.5 g of $KMnO_4$ per L of butyronitrile (BN). After cooling, BN was recovered by distillation under N_2 reduced pressure. The middle fraction of the second distillation was dried over activated alumina. Before use the Al_2O_3 was activated at 300–350 °C in vacuo over P_2O_5 for ca. 10 h. Tetrabutylammonium perchlorate was obtained from Fluka (purrissimum quality) and dried in vacuo at 100 °C over P_2O_5.

Electrochemical Apparatus. The measurements were carried out with a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a PAR Model 179 digital coulometer and the PAR 175 universal programmer. The PAR 179 digital coulometer provided a positive feedback compensation for ohmic drop between the working and the reference electrode. The results were recorded on a X/Y recorder.

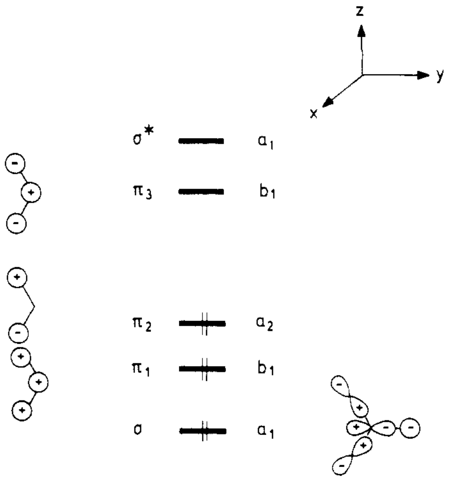
For cyclic voltammetry a cell with a three-electrode configuration similar to that of Van Duyne and Reilly[13] was used. The working electrode was a platinum disk electrode, the reference electrode a saturated calomel electrode (SCE). The distance between the working electrode and the tip of the Haber–Luggin capillary probe was about 1 mm, to minimize the *ir* drop. If necessary, positive feedback compensation was applied. A platinum wire served as the counter electrode.

Cyclic Voltammetry. All electrochemical measurements were carried out at 25 °C in butyronitrile solutions with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Before each measurement the Pt disk was polished with alumina (0.5 μm). The solution was purged with dried argon in order to remove oxygen. The peak potentials were always reproducible to within ±50 mV.

All values of electrode potentials reported in this work refer to the SCE. The liquid junction potential between the aqueous reference electrode and the butyronitrile solution was assumed to be constant and not taken into consideration.[14]

Results and Discussion

a. Bonding in Parent Bis(methylene)phosphorane. We will begin with a discussion of bonding in parent **2**. Within C_{2v} symmetry it possesses an allylic π-system (π_1–π_3). Below (above) these orbitals is a σ (σ*) orbital. The π orbitals form the frontier orbitals and are occupied by four electrons. On this basis **2** is isoelectronic to an allyl anion. Alternatively, the bonding situation in **2** may be described by Rundle's four-electron three-center bond model.[15] The π-space as frontier orbitals is confirmed by the results of the semiempirical (MNDO) as well as the ab initio calculations.



To what extent do d orbitals contribute to bonding? In order to answer this question we performed ab initio calculations on parent **2**, using a saturated s,p-basis set. The calculations were performed once with inclusion of d orbitals at the heavy atoms C and P and once without them.[16] The differential values ob-

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(10) The computer program used is described by Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157.

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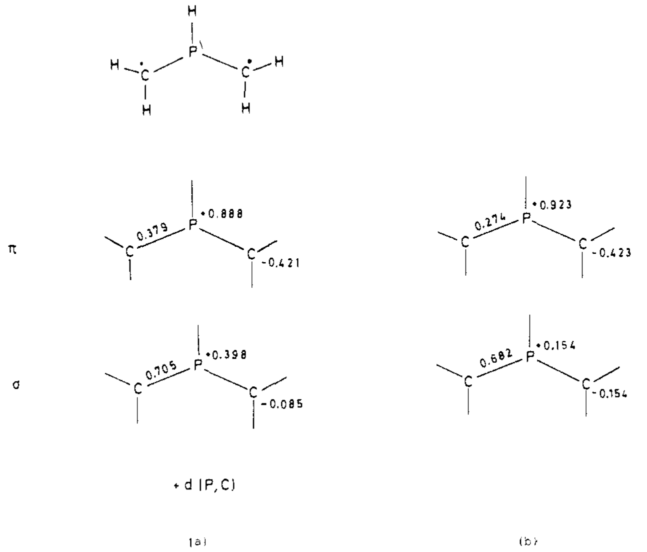
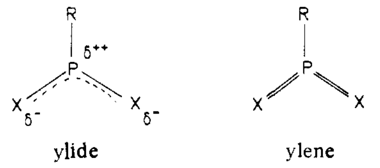


Figure 1. Mulliken population analyses of parent bis(methylene)phosphorane at an ab initio double-ζ level (a) with (basis II) and (b) without (basis I) inclusion of *d*-functions at the atoms C and P. Net charges at atoms and populations between bonds, either for the total π-space or the total σ-space.

tained from the Mulliken population analysis reveal the amount of d-orbital participation. The results achieved are summarized in Figure 1.

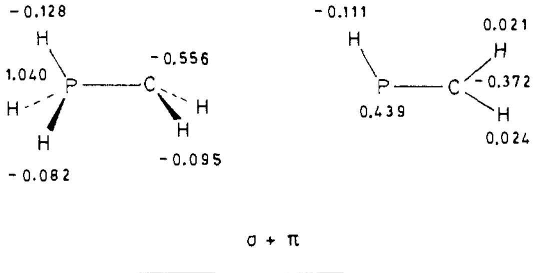
The central phosphorus atom possesses five valence electrons. Two will enter the π-space while the other three are used for the formation of the σ-bonds. Our results indicate that the π-system is considerably polarized. The phosphorus carries positive and the carbon atoms carry negative charge. Almost one electron is taken off the central position and shifted toward the terminal carbon atoms. In comparison, in the σ-core the carbon atoms are only slightly more negative than phosphorus. The inclusion of d orbitals in the wave function affects the overlap populations only to a minor extent. Thus they are of negligible importance for the π-bond description in **2**.

In principle, the bonding in **2** can be ascribed for by a ylene structure or alternatively by the ylide structure, described as follows. Our findings are clearly in favor of the ylide structure,



as is the case of methylenephosphorane.[2]

Next we will relate bonding in **2** to that in **1** and **3**. Ab initio calculations of the same quality (basis II) were performed; the geometrical parameters were chosen according to the literature. The results of the corresponding Mulliken populations are as follows: Again, only the parent systems with hydrogens at the heavy atoms were investigated. In **1** the carbon atom carries even more negative charge than in **2**. The least polar system is methylenephosphane (**3**). Further partitioning of the population into contributions to the π-space and the σ-space reveals an essentially unpolar π-bond.[17] In **2** the phosphorus is most positive (σ + π) compared with **1** and **3**.



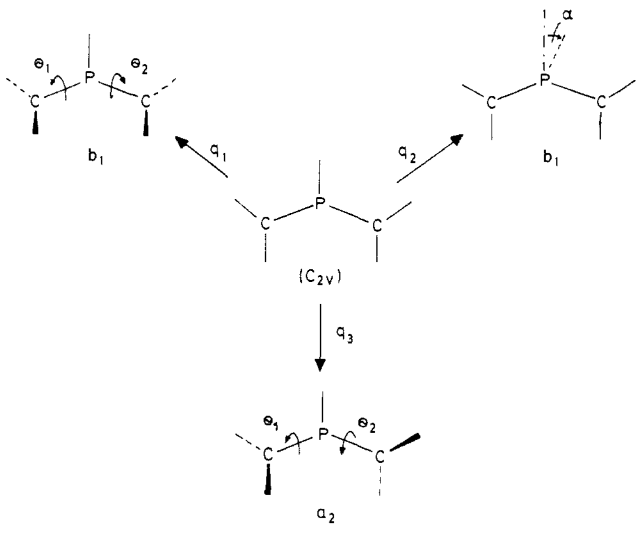


Figure 2. Modes for second-order Jahn–Teller distortion in bis(methylene)phosphorane.

Similar trends are observed for the overall d-orbital populations at phosphorus. They decrease continuously from **1** to **3**: **1** (0.256), **2** (0.249), and **3** (0.108). In all cases studied here, the overall d orbital populations are negligibly small, and the d orbitals do not participate in bonding. Rather, they act as polarization functions.[18]

b. Jahn–Teller Distortion of the Ground-State Hypersurface. Despite the fact that in phosphine, PR_3, the phosphorus adopts a strongly pyramidal conformation,[19] in **2** the ligands at phosphorus are all in one plane. We will now discuss the ground-state hypersurface of **2** on the basis of the second-order Jahn–Teller (SOJT) effect.[20] Accordingly, the energy profit due to distortion of a structure is given by expression 1, where *U* is the nuclear–nuclear and nuclear–electronic potential energy and *Q* the displacement along the reaction coordinate for distortion to lower symmetry.

$$E^{(2)} = \sum_{k} \frac{\left[\left\langle \psi_o \left| \frac{\partial_U}{\partial_Q} \right| \psi_k \right\rangle Q\right]^2}{(E_o - E_k)} \qquad (1)$$

ψ_o and ψ_k (E_o and E_k) refer to the wave functions (orbital energies) of the unperturbed system. The integral $\langle\psi_o|\partial_U/\partial_Q|\psi_k\rangle$ will be nonzero only if condition 2 is fulfilled; that

$$\Gamma_{\psi_o} \times \Gamma_{\psi_k} \subset \Gamma_Q \qquad (2)$$

is, only those excited states whose symmetry matches correctly with those of the ground state and the reaction coordinate can be effective.

First consider planar PH_3[21] (D_{3h} symmetry). The frontier orbitals p and σ* belong to a_2'' and a_1'. Mixing of both orbitals is obtained by a vibration $a_2'' \times a_1' = a_2''$, which corresponds to the force inducing pyramidalization at phosphorus.

We will not adopt this picture for the various possible distortion modes of **2**. Mathematically, the nuclear displacements that are

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(16) The parameters (bond lengths in angstroms, bond angles in degrees) were chosen as follows: Methylenephosphorane, Lischka, H. *J. Am. Chem. Soc.* **1977**, *99*, 353. Methylenephosphane, Hopkinson, M. J.; Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Chem. Soc., Chem. Commun.* **1976**, 513. Bis(methylene)phosphorane (C_{2v} symmetry): PC = 1.650, PH = 1.420, and CH = 1.090 Å; ∠ CPC = 130.0°, ∠ HCH = 120°.

(17) Schoeller, W. W. *J. Chem. Soc. Chem. Commun.* **1985**, 334.

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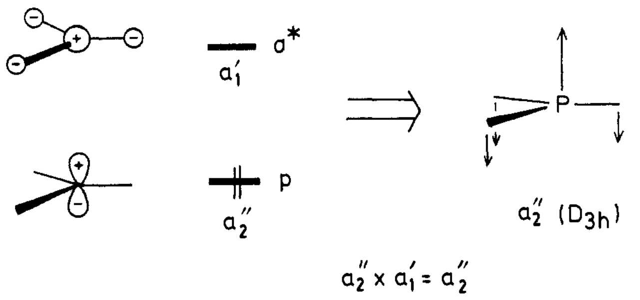


shown in Figure 2 can be expressed as

$$q_1 = \frac{1}{2^{1/2}}(\theta_1 + \theta_2) \tag{3}$$

$$q_2 = \alpha \tag{4}$$

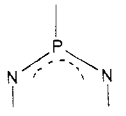
$$q_3 = \frac{1}{2^{1/2}}(\theta_1 - \theta_2) \tag{5}$$

where θ_1 and θ_2 refer to rotational angles and α to the pyramidalization angle at phosphorus. Since the q_1 and q_2 modes lead to the same symmetry, they will be coupled. The various geometrical distortions refer to b_1 (q_1, q_2) or a_2 (q_3) within C_{2v} symmetry.

Since the energy differences between the occupied and unoccupied orbitals are much larger than those in planar PH_3, the situation for the evaluation of the various SOJT nuclear distortion modes is more complex. For the b_1 vibration a symmetric (a_1) σ-type orbital (σ,σ^*) must interact with a symmetric (b_1) π-type orbital (π_3, π_1). Alternatively, the a_2 vibration, which causes conrotation of the methylene groups, involves the mixing of the antisymmetric π_2 (a_2) orbital with σ^* (a_1). One must note that the HOMO–LUMO interaction itself refers to $a_2 \times b_1 = b_2$, which does not cause any symmetry lowering by rotation of the methylene groups.

On the basis of these symmetry arguments it is difficult to predict which vibrational mode will cause symmetry breaking from the C_{2v} structure. In order to put the qualitative model on firmer ground we performed energy-optimized MNDO calculations on various substituted bis(methylene)phosphoranes. The results are summarized in Table I. In all cases the deviations from C_{2v} symmetry are small. The largest effect on the pyramidalization is obtained for the case R = F. However, with respect to the energy, the forces which induce pyramidalization at phosphorus are weak. Disrotation is also observed for methyl substitution at the carbons. On the other hand the more bulky silyl groups cause conrotation in order to minimize steric repulsion.

We have also studied pyramidalization in the related structures, bis(imino)phosphorane[22] (**4**) and bis(oxo)phosphorane[23] (**5**).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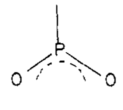
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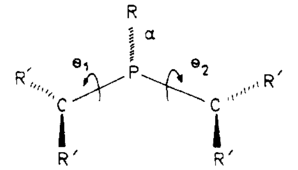
There the preference for the planar conformation is increased. The electronegative atoms at the phosphorus (NH < O) withdraw π-electron density and deplete electron density at the central atom. This is in conformity with quantum chemical calculations on this system (not published here).

c. Electrocyclic Ring Closure. At the end of the theoretical part of this publication on bis(methylene)phosphoranes we analyze the ring closure of **2** to **2a**. In one case[5] the stereochemical investigations revealed a conrotatory ring closure. Since the π-system in **2** is very polar, one expects considerable substituent

Table I. Geometrical Parameters for Various Substituted Bis(methylene)phosphoranes



R[a]	R'[a]	θ_1,[b] deg	θ_2, deg	α,[c] deg	ΔE,[d] kcal/mol
H	H	29	29	41	0.8
F	H	43	44	50	3.9
NH_2[e]	H	30	31	36	1.3
CH_3	H	12	12	17	0.1
H	CH_3[f]	56	26	53	
H	SiH_3[f]	1	-4	2	

[a] R (R') are the substituents at phosphorus (carbon atoms). [b] θ_1 and θ_2 are the rotational angles of the methylene groups. [c] α^4 is the pyramidalization angle at phosphorus. [d] ΔE is the energy differences between the planar (C_{2v}) structures and the equilibrium geometries. [e] Planar (sp^2) conformation at N assumed. [f] Disubstitution at each carbon atom.

Table II. Energy Differences between **2** and **2a** ($\Delta H_f(\mathbf{2}) - \Delta H_f(\mathbf{2a})$) for the Various Substituted Structures

R[a]	R'[b]	ΔE, kcal/mol
H	H	73.3
F	H	88.3
NH_2	H	79.2
CH_3	H	69.5
SiH_3	H	64.5
H	CH_3	47.3
H	SiH_3	49.3

[a] R is at phosphorus. [b] R' is at the carbon atoms (disubstitution at each C).

Table III. Peak Potentials for Oxidation and Reduction of Various Substituted Bis(methylene)phosphanes[a]

R[b]	$E_p^{ox,2}$, V	$E_p^{red,1}$, V
Ph_2CH-	1.10	-1.93
t-Bu-	0.94	-1.88
PhCH=CH-	1.06	-1.45
PhO-	1.38	-2.15
PhS-	1.24	-1.75
i-PrS-	1.19	-1.97
MeEtCH-	0.95	-2.03
Et_2N	1.24	-2.80

[a] V = 100 mV/s; potentials are at times in reference to SCE. [b] R is the substituent at phosphorus, at each carbon atom are two trimethylsilyl groups.

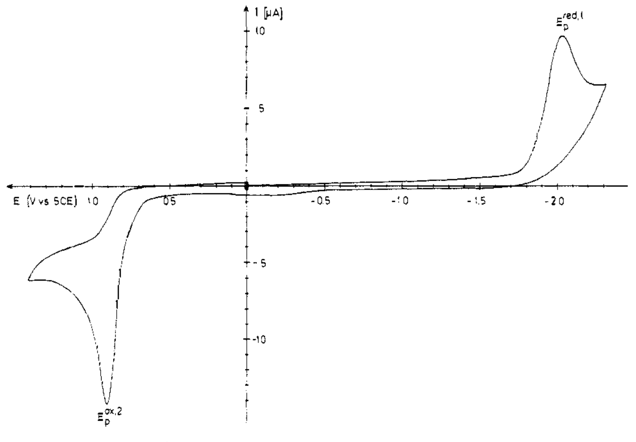


Figure 3. Cyclic voltammogram of **2** (R = EtMeCH; R' = trimethylsilyl, two at each carbon atom) in butyronitrile/0.1 M Bu_4NClO_4 at a Pt electrode; $c = 4.82 \times 10^{-3}$ mol/L, v = 100 mV/s.

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effects on the energy differences between **2** and **2a**. To put this assertion on firmer ground we have calculated the structures **2** and **2a** for a variety of substituents. The results are collected in Table II. As expected, the closed form, **2a**, is always the most stable entity on the electronic hypersurface. The substituent effects on the energy difference between **2** and **2a** are considerable. Electronegative substituents at phosphorus increase the preference for the closed form. On the other hand silyl groups at the carbon atoms are in strong favor of the open form, **2**. This is due to the strong electron-withdrawing ability of silyl groups. In other words the substituent effects are strong for **2** and weak for **2a**.

d. Electrochemical Investigations. Finally, our study will be completed by electrochemical investigations on **2**. A typical cyclic voltammogram for a derivative of **2** is shown in Figure 3. The anodic oxidations as well as the cathodic reductions are irreversible. Even at temperatures of −100 °C the redox reactions remain irreversible. For a variety of substituted **2** the redox potentials were recorded. They are listed in Table III. The oxidation potentials in the various structures remain almost constant. They vary in the range of 0.4 V. According to the previous investigations the HOMO in **2** refers to the nonbonding π-MO of an allyl system. On this basis the various substituents at phosphorus do not exert a considerable effect on the oxidation potential of **2**, especially since the substituents at the carbon atoms are the same. On the contrary, the substituent effects on the reduction potentials are much larger. Consider the amino-substituted bis(methylene)phosphorane. Its value for the reduction potential is considerably increased. Since the LUMO of an allyl system bears a large coefficient at phosphorus, a substituent which is capable of π-conjugation, e.g., an amino group, lifts the energy level.[24] Hence the electrochemical reduction will become disfavored.

A special case is also provided for **2**, R = (PhCH=CH—). This substituent strongly lowers the reduction potential due to an extension of the π-system. At the same time the electrochemical reduction becomes reversible.[25]

Conclusions

Our findings can be summarized as follows: (1) The bis(methylene)phosphoranes possess an allyl system occupied by four electrons. The polar character of the π-bond is larger than that in methylenephosphane and comparable with that in methylenephosphorane. The d-orbital participation to bonding is negligible, as in methylenephosphorane. The central phosphorus donates almost one electron toward the peripheral carbon atoms. Hence it becomes strongly electropositive.

(2) The π-bonds in **2** are weak, which causes a Jahn–Teller distortion of the electronic hypersurface. The tendency for pyramidalization at phosphorus increases by introduction of electronegative substituents at phosphorus. However, it also decreases with increasing electronegativity of the π-ligands (which form the allyl system) at the central atom (bis(methylene)phosphorane > bis(imino)phosphorane > bis(oxo)phosphorane). The latter findings are in contrast to the common belief that electronegative substituents at phosphorus (AB_3 system) increase its inversion barrier.

(3) The trends for pyramidalization parallel those for the ring-closure reaction of **2** to **2a**. Silyl groups (or to a less extent methyl) at carbon stabilize the ylide **2** more than **2a**, and the energy difference between both structures decreases. At the same time these substituents promote planarity at the phosphorus atom.

(4) The frontier orbital in **2**, a nonbonding π_2 orbital as HOMO and π_3 as LUMO, is confirmed by electrochemical investigations. For the case of reduction, which measures the LUMO energy, the peak potentials depend strongly on the nature of the substituents attached to the phosphorus atom. In most cases the oxidation and reduction processes are irreversible.

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(24) The situation is similar to that in singlet carbenes. There the LUMO is raised in energy with decreasing electronegativity of the ligands, i.e., in the order $CF_2 < C(OR)_2 < C(NR_2)_2$. Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 698. Schoeller, W. W. *Tetrahedron Lett.* **1980**, 1505.

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