Electrochemical Investigations on Methylenephosphines and Related Systems

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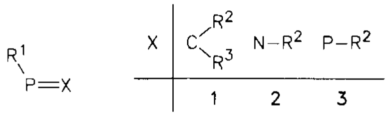
Received June 25, 1990

Key Words: Methylenephosphines / Voltammetry, cyclic

Electrochemical investigations on a selection of methylenephosphines **1** and related systems are reported. They are shown to possess an irreversible oxidation and reduction wave. An exception is diaminodiphosphene, which reversibly forms a radical anion. A relative ordering of frontier orbitals is possible, based on the redox properties of these systems.

The remarkable elaboration of the synthetic utility of the chemistry of P(III) double-bond systems, methylenephosphines **1**[1] and iminophosphines **2**[2], forms one of the most pleasing chapters in modern inorganic chemistry. The P(III) double-bond systems, **1**–**3**, reveal an ambident behaviour, due to two energetically closely spaced occupied frontier orbitals[3].

Scheme 1



1	a	b	c	d	e
R^1	*t*Bu	NH*t*Bu	NEt_2	$N(SiMe_3)$*t*Bu	TMP[a]
R^2	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$
R^3	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$

1	f	g	h	i
R^1	O*t*Bu	S*tBu*	Cl	*t*Bu
R^2	$SiMe_3$	$SiMe_3$	$SiMe_3$	H
R^3	$SiMe_3$	$SiMe_3$	$SiMe_3$	*t*Bu

[a] TMP: 2,2,6,6-tetramethylpiperidyl

2	a
R^1	*t*Bu
R^2	*t*Bu

3	a	b
R^1	$N(Si$*t*$BuMe_2)_2$	C_5Me_5
R^2	$N(Si$*t*$BuMe_2)_2$	C_5Me_5

This can be seen in the plethora of metal complexes of methylenephosphines **1**, iminophosphines **2**, and diphosphenes **3**[4–6]. In addition, iminophosphines **2** show distinct self-addition behaviour[7] alternatively leading either to [2+1] or [2+2] cycloadducts.

The variety in chemical behaviour of these new classes of compounds raises the question of frontier-orbital energies, i.e., their electron demand[8]. This problem will be dealt with in the present report. We present in detail the first electrochemical investigations of a selection of phosphorus double-bond systems, especially of methylenephosphines **1**. We will relate our findings to substituted ethenes, i.e., to typical electron-rich (enamines) and electron-poor (tetracyanoethene) olefins.

Results and Discussions

Electrochemical Investigations

A typical cyclic voltammogram of a methylenephosphine **1** is shown in Figure 1. The anodic oxidation as well as the cathodic reduction were irreversible. This is a common feature of all methylenephosphines **1**. Even at temperatures of −100°C the redox reactions remain irreversible. The peak potentials for various substituted methylenephosphines **1** are collected in Table 1.

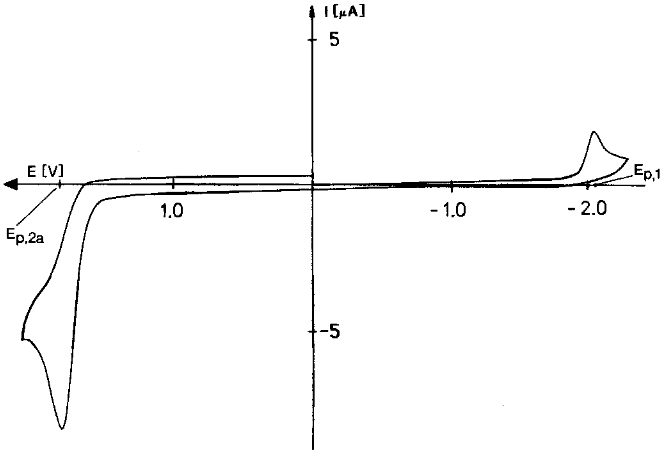


Figure 1. Cyclic voltammogram of **1a** in butyronitrile/0.1 M Bu_4NBF_4 at −100°C; c = 5.49 mmol/l, v = 100 mV/s

For completeness we include the first vertical ionization potentials[9] in Table 1.

To a first-order approximation, the reduction and oxidation potentials are a quantitative measure of the frontier-orbital energies of HOMO and LUMO, even though the

Table 1. Peak potentials for reduction $E_{p,1c}$ and oxidation $E_{p,2a}$ and ionization potentials $I_{p,1}$ of various substituted methylenephosphines **1**; measured in butyronitrile/0.1 M Bu_4NBF_4 at −100°C, concentration 1−5 mmol/l, v = 100 mV/s

Compound	$E_{p,1c}$ [V]	$E_{p,2a}$ [V]	$I_{p,1}$ [eV]
1a	−2.06	1.83	8.10
1b	−2.67	1.56	7.74
1c	−2.51	1.35	7.55
1d	−2.38	1.40	7.47
1e	−2.37	1.07	7.26
1f	−2.47	2.24	8.36
1g	−2.05	1.95	7.94
1h	−1.82	2.94	9.22
1i	−2.73	2.43	8.74

measured peak potentials refer to irreversible processess[10]. Hence, one expects a linear relationship between the two quantities, although they are obtained by different spectroscopic techniques. A plot of the first vertical ionization potentials versus the anodic oxidation peaks is shown in Figure 2. The correlation coefficient between both quantities is r^2 = 0.976. In other words, the anodic oxidation potential $E_{p,2a}$ is a reliable measure of the relative HOMO energy of these compounds.

The peak potentials (Table 1) depend strongly on the substituents attached to the π system. The effects on the HOMO and the LUMO energies are as expected on the basis of Hammett constants for substituents[11]. Halogen substitution lowers the energy of both frontier orbitals, of the HOMO and the LUMO. Hence, **1h** is most difficult to oxidize and most easy to reduce. Amino groups at the phosphorus atom, e.g., compounds **1b**−**1d**, do the opposite, they enrich the π system. The HOMO and LUMO are raised in these compounds. The structures **1a** versus **1i** differ in silyl substitution versus alkyl substitution. In fact, a trimethylsilyl group strongly raises the HOMO and lowers the LUMO when compared with its corresponding alkyl derivative. The data also show evidence for steric effects, acting on the conjugating amino group. Accordingly, its conjugation falls off in the order **1b** > **1c** > **1d** > **1e**.

For comparison, we have also recorded cyclic voltammograms of other related π-bonded systems (Table 2).

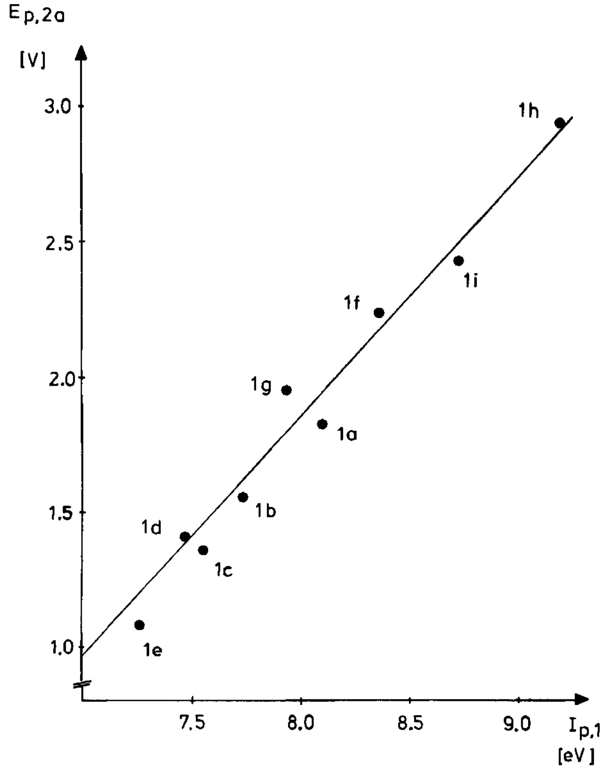


Figure 2. Correlation of oxidation potentials $E_{p,2a}$ of methylenephosphines **1** with their first vertical ionization potentials $I_{p,1}$

Table 2. Peak potentials for reference π-bond systems; measured in dichloromethane, concentration 3−7 mmol/l, v = 100 mV/s

Compound	$E_{p,1c}$ [V]	$E_{p,2a}$ [V]
2a	−2.16	[b)]
3a	−1.75[c)]	1.04
3b	−1.77	0.77[b)]
TCNE[d)]	−0.82[c)]	0.27[c)]

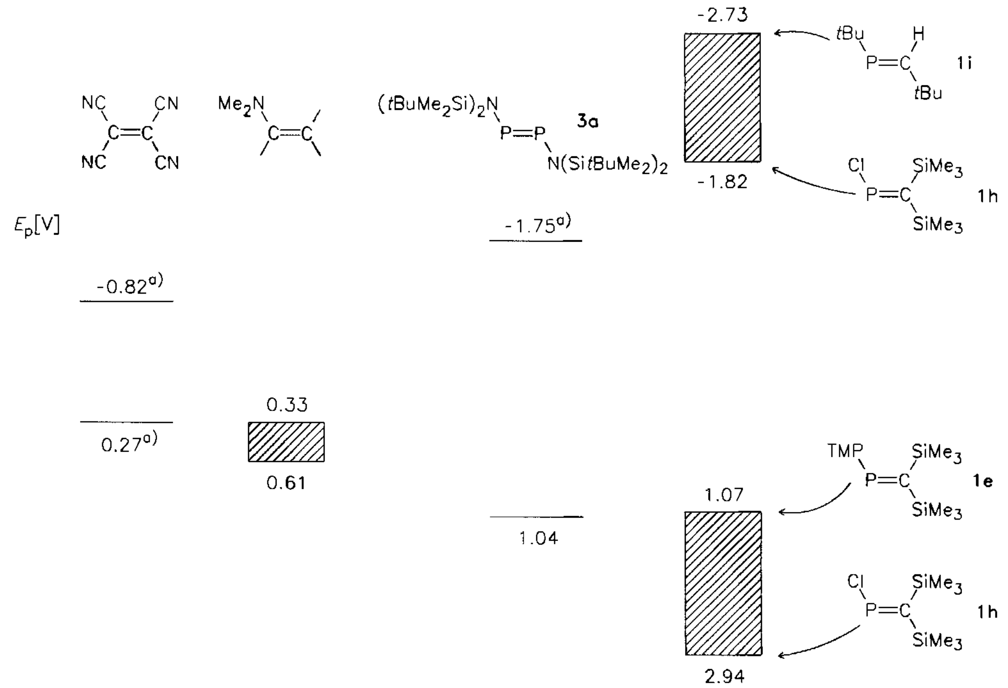
[a)] Produced in the electrochemical cell by photolysis of the dimer. — [b)] Unequivocal assignment of the peak potentials not possible. — [c)] Nernst potentials ($E°$); measured in butyronitrile at 25°C. — [d)] TCNE: tetracyanoethene.

Table 2 includes one dialkyliminophosphine **2** and two diphosphenes **3**. It must be noted that these compounds were measured under different experimental conditions. Hence, the peak potentials are not strictly comparable among each other. However, the diphosphenes **3** are easier to oxidize and to reduce than the methylenephosphines **1**. The diphosphene **3a** also reversibly forms an anion radical at room temperature. The oxidation potential of the iminophosphine **2a** could not be measured. Since it is known that it readily dimerizes at room temperature to its [2+1] adduct[12], it had to be produced at −80°C in the electrochemical cell by photolysis of the dimer. The oxidation waves of the dimer and the monomer overlap. Hence, an unequivocal assignment of the oxidation wave of the iminophosphine **2a** by the present technique is not possible.

A comparison with the electronic properties of carbon−carbon double-bond system is shown in Scheme 2.

Enamines are typical electron-rich olefins. Their first ionization potentials lie in the range of 7.0 to 7.7 eV[13], depending on the various π-bonded substituents. At the same time, their (totally irreversible) oxidation potentials appear at 0.33 to 0.61 V (in acetonitrile at room temperature)[13]. It is also interesting to compare them with tetracyanoethene (TCNE), a classical dienophile in [4+2] cycloaddition reactions. In butyronitrile it shows two reversible waves for oxidation as well as for reduction. The Nernst potentials are $E°$ = 0.27 V for oxidation and $E°$ = −0.82 V for reduction. Thus, on the basis of the electrochemical scale, its LUMO is much lower in energy than that of the diphosphenes **3** (see Table 3)

Scheme 2



$^{a)}$Nernst potential.

and of iminophosphine **2a** (−2.16 V). At the same time TCNE is much easier to oxidize than the methylenephosphine **1i**. Although the experimental conditions for the two series of electrochemical measurements are not strictly comparable with each other, one may conclude that the methylenephosphines **1** are less electron-rich than enamines.

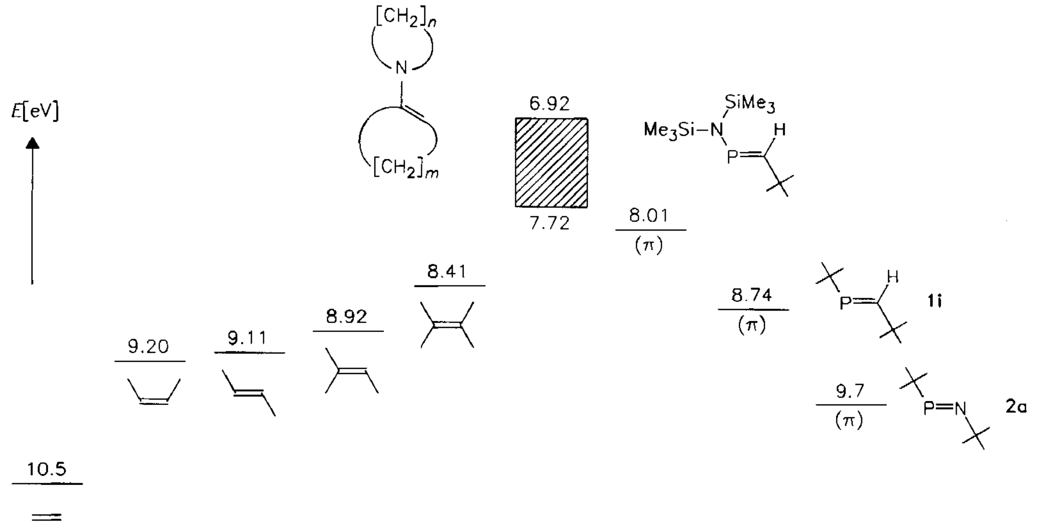
Frontier Orbitals, Electron Demand

In the language of frontier-orbital theory[14], the electron demand of a π bond is defined by its HOMO and LUMO energy, and the energy values for the P(III) double-bond systems may be compared with typical carbon−carbon double bonds (Scheme 3).

The data summarized in Scheme 3 are taken from the literature[15]. *trans*-2-Butene is slightly higher in its π-ionization potential than the methylenephosphine **1i**. The enamines possess lower ionization potentials when compared with amino-substituted methylenephosphines **1**. In other words, an amino group at the phosphorus atom of the P(III) double bond enriches less effectively than when acting on a carbon−carbon double bond. This is due to less overlap <n|π> of the nonbonding orbital at the nitrogen atom with the neighbouring π bond in the former compared with the latter type of bond.

This work was supported by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft.*

Scheme 3



Experimental

Materials: Samples of the various P(III) double-bond systems were kindly provided by Prof. *E. Niecke* (University of Bonn) and Prof. *P. Jutzi* (University of Bielefeld). These compounds were prepared according to literature procedures.

In the electrochemical experiments, butyronitrile or dichloromethane were used as solvents. Butyronitrile (for synthesis; Merck) was purified according to the method of van Duyne and Reilly[16]. It was heated twice 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 1 of butyronitrile. After cooling, the solvent was recovered by distillation under N_2 and reduced pressure. The middle fraction of the second distillation was dried with activated alumina (Woelm). Dichloromethane was distilled from CaH_2 and dried with activated alumina (Woelm).

Tetrabutylammonium tetrafluoroborate (99%) was obtained from Aldrich, recrystallized from ethanol/water, and dried in vacuo at 80°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 a PAR 175 universal programmer. The PAR digital coulometer provided positive feedback compensation for ohmic drop between the working and the reference electrode. The results were recorded with an *X/Y* recorder.

For cyclic voltammetry we have constructed a special cell for the measurement of these extremely air- and moisture-sensitive compounds (Figure 3). It allows investigations at very low temperature.

The three-electrode configuration is similar to that of Van Duyne and Reilly[16]. The working and reference electrode are thermally isolated from the solution by a long electrolyte bridge. The cell is cooled with N_2 which had been precooled in a heat exchanger. The temperature was constant in the cell within ±1°C. The working electrode was a platinum disk electrode (Bioanalytical Systems), the reference electrode a saturated calomel electrode (SCE). The distance between the working electrode and the tip of the Haber-Luggin probe was ca. 1 mm, to minimize the uncompensated resistance (IR drop). If necessary, positive feedback compensation was applied. A platinum wire served as the counter electrode.

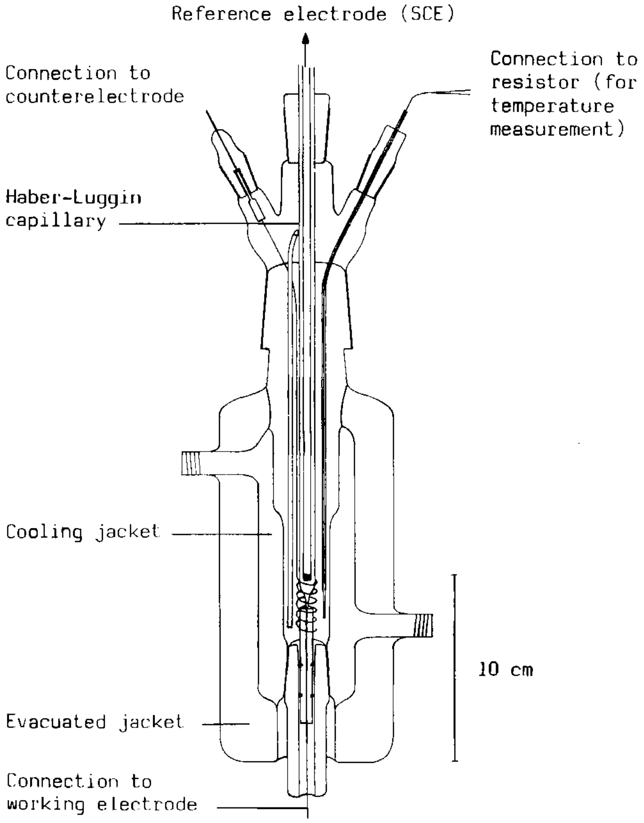


Figure 3. Electrochemical cell for the low-temperature measurements

Cyclic Voltammetry: The iminophosphine **2a** was measured in dichloromethane with 0.1 M tetrabutylammonium tetrafluoroborate at −80°C. The other P(III) double-bonded compounds were measured at −100°C in butyronitrile/0.1 M tetrabutylammonium tetrafluoroborate solutions. Before each measurement the platinum 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 reported in this work refer to the SCE. The liquid junction potential between the aqueous reference electrode and the butyronitrile was assumed to be constant and not taken into consideration[17]. In reference to these investigations the standard potential of ferrocene was +0.53 V (at room temperature).

CAS Registry Numbers

1a: 78928-40-2 / **1b**: 112474-49-4 / **1c**: 112474-51-8 / **1d**: 89982-44-5 / **1e**: 91117-85-0 / **1f**: 112489-72-2 / **1g**: 112474-48-3 / **1h**: 79454-85-6 / **1i**: 99278-17-8 / **1j**: 131154-37-5 / **2a**: 95552-76-4 / **3a**: 131154-38-6 / **3b**: 104598-67-6 / TCNE: 670-54-2 / CH_2Cl_2: 75-09-2 / Bu_4NBF_4: 429-42-5 / butyronitrile: 109-74-0

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