J. Org. Chem. 1983, 48, 4206-4209

Organophosphorus Redox Systems

Wolfgang Kaim,* Ulrike Lechner-Knoblauch, Peter Hänel, and Hans Bock

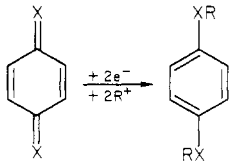
Chemistry Department, J. W. Goethe Universitaet, Niederurseler Hang, D-600 Frankfurt/Main, West Germany

Received February 16, 1983

Redox systems involving R_2P-, $R_2P(X)$-, and R_3P^+-substituted benzenes and biphenyls have been studied by cyclic voltammetry in dimethylformamide. The first one-electron reduction was found to be reversible in several instances, and stable radical anions, cations, and uncharged radicals were detected by high-resolution electron spin resonance. The second reduction step was found to be irreversible in all cases investigated. The electrochemical and spectroscopic data illustrate the considerable difference in acceptor strength between R_2P and R_3P^+ substituents; MO calculations of the radical species give a quantitative measure for this difference and for the overall substituent effects. A comparison is made between the organophosphorus redox systems presented and the quinone/hydroquinone redox systems.

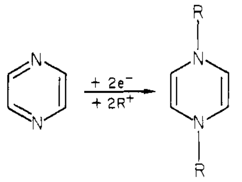
Introduction

Among the most prominent redox/coordination systems are 1,4-perturbed benzenes; this includes the quinone/hydroquinone (eq 1, a), the related quinonediimine/*p*-phenylenediamine (eq 1, b)[1] and the 1,4-diazine/1,4-dihydro-1,4-diazine systems (eq 2).[2] Employing a second-row element as coordinating atom, we present here a novel redox/coordination system that involves phosphane, phosphonium, and ylidic functions at the 1,4-positions of the benzene nucleus (Scheme I).



(1)

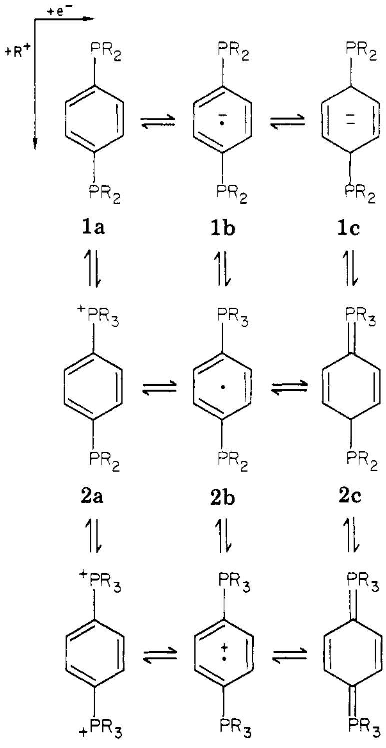
a, X = O
b, X = NR′
R^+, electrophile



(2)

The system shown in Scheme I, R = CH_3, has been studied by electrochemical (CV) and spectroscopic (ESR) techniques. For comparison, we have also examined the reduction behavior of the 1,3-isomers **4a** and **5a**, the phenylogous biphenyl systems **6a** and **7a**, and the perphenyl derivative **8a**; the phosphonium salts were studied in the form of iodides (Scheme II). The data for 1,4-disubstituted benzene systems are also compared to those of the P^V compounds **9a**–**12a**.

Scheme I[a]



[a] R = CH_3.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon or nitrogen and rigorously dried and freshly distilled solvents were used. NMR spectra were determined on a Varian T 60 spectrometer. Elemental analyses were obtained from the microanalytical laboratory, Professor Ried, Frankfurt University.

Electrochemistry. Cyclic voltammetric studies were performed on a PAR 173/175 system by using a glassy carbon working electrode and a saturated calomel reference electrode (SCE), separated from the solution by a diaphragm. DMF (Roth) was dried over molecular sieves (4 Å), was distilled under vacuum, and contained 0.1 M tetrabutylammonium perchlorate (Fluka, recrystallized twice from ethanol). The data in Table I refer to a sweep rate of 0.1 V/s.

Electron Spin Resonance. ESR spectra were determined on a Varian E 9 instrument that included the E 257 variable-temperatuer accessory. The radicals were either generated by alkali metal reduction in THF (phosphanes) or by electrochemical reduction at a mercury cathode in DMF/0.1 M $Bu_4N^+ClO_4^-$ by using a capillary system inside the cavity of the ESR spectrometer.[3] Computer syntheses of theoretical ESR spectra were carried out by using the program ESPLOT.[4] Coupling constants and *g* values were determined in reference to the perylene radical anion in DME.[5]

The preparation of the compounds **1a**,[6] **4a**,[3] **6a**,[3] **8a**,[7] **9a**,[3] **10a**,[6] **11a**,[8] and **12a**[8] has been described earlier.

---

[1] Deuchert, K.; Hünig, S. *Angew. Chem.* **1978**, *90*, 927; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875.

[2] Kaim, W. *Angew. Chem.* **1983**, *95*, 201; Angew. *Chem., Int. Ed. Engl.* **1983**, *22*, 171.

[3] Kaim, W.; Bock, H. *Chem. Ber.* **1981**, *114*, 1576.

[4] Kaim, W.; Bock, H. *J. Organomet. Chem.* **1979**, *164*, 281.

[5] Bolton, J. R. *J. Phys. Chem.* **1967**, *71*, 3702.

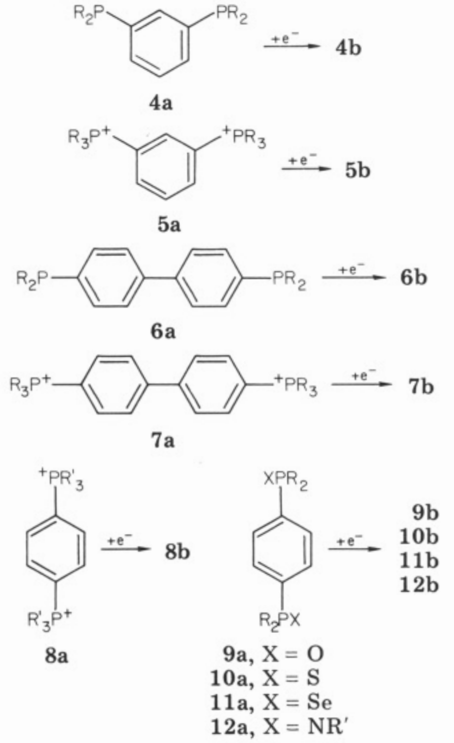
[6] Kaim, W.; Bock, H. *Chem. Ber.* **1978**, *111*, 3843.

[7] Cf. Horner, L.; Munnenthey, G.; Moses, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782.

[8] Kaim, W. *Z. Naturforsch. B* **1981**, *36b*, 150.

0022-3263/83/1948-4206$01.50/0

Scheme II[a]



[a] R = CH_3; R' = C_6H_5.

Phosphonium salts were synthesized in nearly quantitative yields by reacting the corresponding phosphane with a stoichiometric amount of methyl iodide in toluene. Filtration and removal of the solvent under high vacuum afforded colorless iodides which were stored under argon.

1-(Trimethylphosphonium)-4-(dimethylphosphino)benzene iodide (2a): ^{1}H NMR (Me_2SO-d_6, Me_4Si) δ 1.37 (d, 6 H, $J = 2.5$ Hz), 2.25 (d, 9 H, $J = 15$ Hz), 7.65–8.15 (m, 4 H). Anal. Calcd for $C_{11}H_{19}IP_2$: C, 38.83; H, 5.59. Found: C, 38.80; H, 5.50.

1,4-Bis(trimethylphosphonium)benzene diiodide (3a): ^{1}H NMR (Me_2SO-d_6, Me_4Si) δ 2.34 (d, 18 H, $J = 15$ Hz), 8.35 (m, 4 H). Anal. Calcd for $C_{12}H_{22}I_2P_2$: C, 29.89; H, 4.58. Found: C, 29.78; H, 4.56.

1,3-Bis(trimethylphosphonium)benzene diiodide (5a): ^{1}H NMR (Me_2SO-d_6, Me_4Si) δ 2.38 (d, 18 H, $J = 15$ Hz), 7.9–8.5 (m, 4 H). Anal. Calcd for $C_{12}H_{22}I_2P_2$: C, 29.89; H, 4.58. Found: C, 30.07; H, 4.54.

4,4'-Bis(trimethylphosphonium)biphenyl diiodide (7a): ^{1}H NMR (Me_2SO-d_6, Me_4Si) δ 2.34 (d, 18 H, $J = 15$ Hz), 8.0–8.25 (m, 8 H). Anal. Calcd for $C_{18}H_{26}I_2P_2$: C, 38.72; H, 4.66. Found: C, 37.83; H, 4.41.

Results

Cyclic Voltammetry. Electrochemical data from CV measurements in DMF are listed in Table I.

The oxidized members **1a**, **2a**, and **3a** of the redox system shown in Scheme I are stable aromatic compounds. They all undergo reversible one electron reduction to yield the paramagnetic species **1b**, **2b**, and **3b**, however, the mixed derivative **2a** does so only at low temperature. Uptake of a second electron, which leads to carbanionic species, either could not be obseerved (**1c**) or is not reversible under the conditions of measurement (**2c**, **3c**). The potentials of the first reversible reduction in the system (Scheme I) show a considerable increase on going from the bis(phosphane) **1a** via **2a** to the bis(phosphonium) salt **3a**, the difference amounting to 1.1 V.

The isomeric 1,3-substituted benzenes **4a** and **5a** exhibit different features on reduction. Whereas the phosphane **4a** is not reducible electrochemically in the accessible region $E > -2.9$ V, a persistent anion radical **4b** can still be obtained by alkali metal reduction in THF.[3] The bis(phosphonium) salt **5a** accepts an electron at a rather high potential, however, even at low temperatures no persistent one-electron reduction product was observed. The 4,4'-biphenyl compounds **6a** and **7a**, on the other hand, display a behavior similar to **1a** and **3a**. It should be noted that the relation of the first reversible potentials is $E_1(\mathbf{6}) > E_1(\mathbf{1})$ for the phosphanes, but $E_1(\mathbf{7}) < E_1(\mathbf{3})$ for the bis(phosphonium) salts.

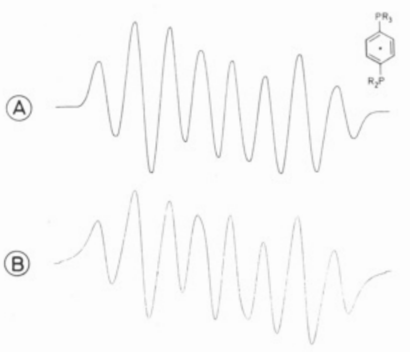


Figure 1. (A) ESR spectrum of radical **2b** in DMF at 213 K. (B) Computer simluation with the data from Table II and a line width of 140 μT.

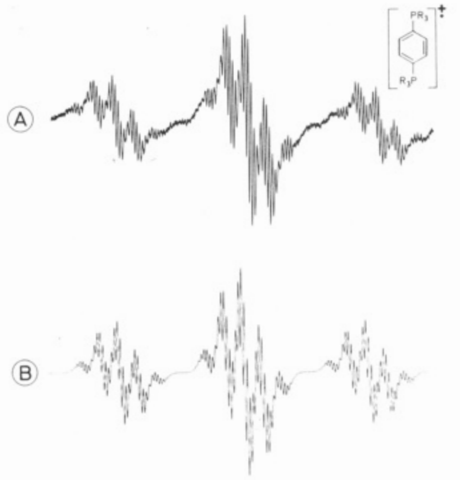


Figure 2. (A) ESR spectrum of radical **3b** in DMF at 243 K. (B) Computer-assisted spectrum synthesis with the data from Table II and line width of 27 μT.

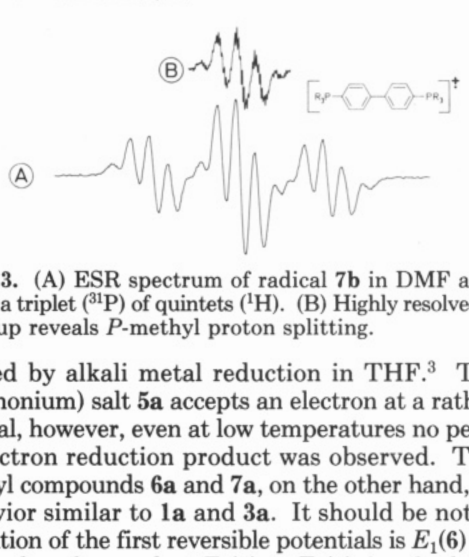


Figure 3. (A) ESR spectrum of radical **7b** in DMF at 213 K, showing a triplet (^{31}P) of quintets (^{1}H). (B) Highly resolved central line group reveals *P*-methyl proton splitting.

The chalcogenides **9a**, **10a**, and **11a** and the bis(phosphanimine) **12a** whose reduction to persistent radical anions was reported earlier[8] all have first reduction potentials in a comparable region; this has already been deduced from intra muros ESR electrolyses.[8]

Electron Spin Resonance. In case of electrochemically reversible one-electron reduction behavior, we could obtain persistent paramagnetic species by intra muros electrolysis inside the cavity of an ESR spectrometer. The spectra of three of these radicals are shown in Figures 1–3; the ESR data, including the marked temperature dependencies of

Table I. Cyclic Voltammetric Data for the Cathodic Reduction of Phosphanes and Phosphonium Salts in DMF/0.1 M Tetrabutylammonium Perchlorate[a]

	first wave			second wave[b]
compd	$-E_{pc}$, V	$E_{pa} - E_{pc}$, mV	i_{pa}/i_{pc}	$-E_{pc}$, V
1a	2.65	70	1.1	not observed
2a I$^-$	2.07	*c*	0	2.65
3a 2I$^-$	1.545	65	1.03	1.87
4a		not observed (see text)		
5a 2I$^-$	1.70		0	2.21
6a	2.33	70	1.1	2.55
7a 2I$^-$	1.60	60	1.0	1.83
8a 2I$^-$	1.16	58	1.03	1.50
8a 2Br$^-$ [d]	1.26	66	1.02	
9a	2.28	110	0.8	2.52
10a[e]	2.16	65	1.0	2.55
11a	2.07	*c*	0	2.36
12a	2.16	80	1.05	2.50

[a] Potential vs. SCE, sweep rate 0.1 V/s. [b] Always irreversible. [c] Irreversible at room temperature, reversible below 260 K. [d] Reference 9, slightly different conditions of measurement. [e] Reference 10.

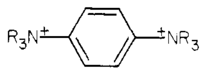
the ^{31}P splittings, are summarized in Table II.

The phosphanes **1a**, **4a**, and **6a** may be reduced by alkali metals in ethers or electrochemically in DMF to yield persistent radical anions.[3] Remarkably, the spectrum of the 1,4-disubstituted benzene **1b** is characterized by temperature-dependent line width alterations[3] due to restricted rotations around the C_{aryl}–P bonds. The phosphonium salts have been reduced electrochemically in DMF. For the systems **3**,[11] **7**, and **8**[9] the corresponding radical cations were detected at room temperature; the uncharged radical **2b**, on the other hand, could only be observed at temperatures below 260 K. In agreement with the electrochemical results, cathodic reduction of the 1,3-bis(phosphonium) benzene **5a** did not yield a detectable radical product at any solution temperature. Radical anions **9b**–**12b** have been analyzed by ESR earlier.[8]

The ESR spectra (Figures 1–3) are generally characterized by the ^{31}P couplings which typically exhibit marked temperature dependence. In addition to the ring proton splittings, one may observe couplings from the substituents at phosphorus under favorable line width conditions; the *g* values of all the phosphane and phosphonium radicals are centered around 2.0028 ± 0.0001.

Discussion

The organophosphorus redox system (Scheme I) differs from the quinone/hydroquinone system (eq 1, a) by the aromatic nature of the oxidized forms instead of the reduced forms. Thus, the redox behavior of the compounds in Scheme I corresponds to the oxidation/reduction chemistry of heterocyclic systems such as those shown in eq 2.[2] Although a redox system such as Scheme I is also conceivable for nitrogen compounds, i.e., N instead of P, this would not constitute a useful redox system because: (i) R_2N substituted aromatics are more readily oxidized than reduced;[6,13a] (ii) R_3N^+ substituted benzenes such as **13a** do not undergo reversible one-electron reduction either.[9] In the case of P substituted π systems phosphane,[3,13b] phosphonium,[9,12,14,15] and phosphane chalcogenide groups can serve as electron acceptors,[16] allowing at least a first, reversible one-electron reduction.



13a, R = CH_3

The instability of the fully reduced molecules (**c**) in the redox system of Scheme I and also in system **8** is attributable to two different causes: First, it is well-known that phosphonium salts have a strong tendency towards cleavage into phosphanes via two-electron addition.[17] Although this process is deferred by resonance stabilization if only one electron is added, it finally becomes dominant on introduction of a second electron.[15] Second, the species

$$R'P^+R_3 \xrightarrow{2e^-} R'^- + PR_3$$

1c, **2c**, and **3c** all contain 8 π electrons in a six-membered ring and should thus exhibit some "antiaromatic" destabilization. Even if such an effect can be overcome by kinetic stabilization,[2,18] it is likely to contribute to the overall instability of the reduced forms (**c**) in the two-step redox system (Scheme I).

The reversibility of the first reduction potential in the cases of the 1,4-bis(phosphonium)benzenes **3a** and **8a** and of the 4,4′-biphenyl derivative **7a** stands in contrast to the irreversible electron uptake of compound **5a**. Such behavior corresponds to the radical stabilities in quinone/hydroquinone redox systems, where 1,2- and 1,4-semiquinones are stable and 1,3-benzosemiquinones are short-lived species.[20]

A comparison of redox potentials for 1,4-benzene and 4,4′-biphenyl systems is illustrative because the one-electron reduction of the biphenyl derivative is easier for the phosphanes but less easy in the case of the phosphonium salts. This latter phenomenon is only found for strong acceptor substituents such as CN[19] and NO_2,[21] an inductive Hückel MO model for the LUMO energies of 1,4-perturbed benzenes and likewise 4,4′-perturbed biphenyls predicts a crossing of orbital energies for a Coulomb integral parameter $h_X = 1$. Only at larger values of h_X is the LUMO energy of the benzene lower than that of the biphenyl derivative so that a reduction becomes easier for the smaller π system.

ESR data for reduced bis(phosphonium) salts have been reported earlier,[15] especially for 1,4-benzene[9,12] or cyclohexadiene systems.[14] The argument[9,12,23] concerning the nature of the R_3P^+/π interaction may be supplemented by the suggestion that species such as **3b** are part of a series of isoelectronic radicals;[11] the spin polarization approach

---

[9] White, C. K.; Rieke, R. D. *J. Org. Chem.* **1978**, *43*, 4638.

[10] Kaim, W.; Hänel, P.; Lechner-Knoblauch, U.; Bock, H. *Chem. Ber.* **1982**, *115*, 1265.

[11] Kaim, W. *Angew. Chem.* **1980**, *92*, 940; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 911.

[12] Rieke, R. D.; White, C. K. *J. Org. Chem.* **1977**, *42*, 3759.

[13] (a) For an exception see: Gerson, F.; Krynitz, U.; Bock, H. *Angew. Chem.* **1969**, *81*, 786; *Angew. Chem., Int. Ed. Ngl.* **1969**, *8*, 767. (b) Gerson, F.; Plattner, G.; Bock, H. *Helv. Chim. Acta* **1970**, *53*, 1629.

[14] Rieke, R. D.; Copenhafer, R. A.; Aguiar, A. M.; Chattha, M. S.; Williams, Jr., J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 1130.

[15] Berdnikov, E. A.; Tantasheva, F. R.; Morozov, V. I.; Ilyasov, A. V.; Vafina, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 803.

[16] Cf.: Schiemenz, G. P. *Angew. Chem.* **1968**, *80*, 559; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 544.

[17] Cf., e.g.: Savéant, J. M.; Binh, S. K. *J. Org. Chem.* **1977**, *42*, 1242 or Pardini, V. L.; Roullier, Utley J. H. P.; Webber, A. *J. Chem. Soc. Perkin Trans. 2* **1981**, 1520.

[18] Kaim, W. *J. Am. Chem. Soc.* **19833**, *105*, 707.

[19] Bartak, D. E.; Houser, K. J.; Rudy, B. C.; Hawley, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7526.

[20] Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 4302.

[21] Lechner-Knoblauch, U., Thesis, University of Frankfurt, 1983.

[22] Heilbronner, E.; Bock, H. "The HMO-Model and its Application"; Wiley-Verlag Chemie: London/Weinheim, 1976; p 156.

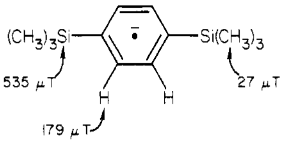
[23] Symons, M. C. R. *Electron Spin Reson.* **1979**, *5*, p 153; **1980**, *6*, p 112.

Table II. Electron Spin Resonance Data for Reduced Phosphanes and Phosphonium Salts[a]

radical	solvent	a_P (213 K)	da_P/dT (μT/K)	$a_H^{PCH_3}$	a_H^{CH}
1b Na$^+$ [b]	THF	562	−1.9	≤10	180
2b	DMF	860 (P_1) 630 (P_4)	−1.5 (P_1) −2.5 (P_4)	≤50	330 ($H_{2,6}$) ≤70 ($H_{3,5}$)
3b I$^-$ [c]	DMF	1410	−1.2	30	194
3b Br$^-$ [d]	DMF	1508[c]	e	35 (CH_2)[d]	213
8b I$^-$	DMF	1210	−1.2		195[f]
8b Br$^-$ [g]	DMF	1194[g]	e		189
6b Na$^+$ [b]	THF	348	−1.3	9.4	224 (H_2) ≤3 (H_3)
7b I$^-$	DMF	920	−0.7	20	190 (H_2) ≤20 (H_3)

[a] Coupling constants in μT. [b] Reference 3. [c] Cf. ref 11 for room temperature data. [d] $R = C_2H_5$, ref 12, 226 K. [e] Not reported. [f] a_C = 870 μT, 600 μT. [g] Reference 9, temperature not reported.

towards R_3Si substituted benzene radical anions[24] may then be transferred to R_3P substituted benzene radical cations. Even the "peripheral"[12] alkyl group splittings are comparable in both cases (cf. **14b**); this suggests a hyperconjugative (σ/π) rather than a "conjugative"[9,12] interaction.[23a]



14b

Although both substituents are electron acceptors, there are significant differences between the ESR parameters for the R_2P and R_3P^+ groups. The ^{31}P coupling constants are 2–3 times larger in the latter case, an effect of the significantly different geometries. The temperature dependence, however, is greater for the ^{31}P splitting in the phosphane radicals, where the substituent has more space available for rotatory and vibratory motion (cf. also the restricted rotation in **1b**[3]).

The ring hydrogen coupling constants are in good agreement with spin populations as calculated from Hückel MO theory via[25] the McConnell equation:

$$a_H = Q\rho^\pi = Qc_C^2$$

An interesting case for spin density considerations is the radical **2b**. If the coupling constants of the α nuclei are taken as a measure for the spin distribution in a spin polarization model, one can reproduce the experimental results by assuming a large difference in acceptor strength between the weak (R_2P) and the strong acceptor (R_3P^+). An HMO correlation starting out with the radical **1b** shows the experimentally observed trends as a function of the increasing acceptor strength of one substituent: decrease of the unpaired electron density in positoins 4, 2, and 6, increase for the positions 3 and 5, and a slight increase in position 1 (Figure 4).

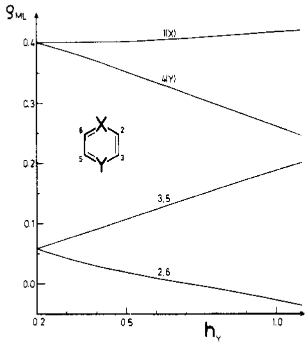


Figure 4. Hückel MO–McLachlan[26] spin densities δ_{ML} for a 1,4-perturbed benzene system; h_x = 0.2, k_{CX} = k_{CY} = 1.0; McLachlan parameter λ = 1.2.

Summarizing, simple redox/coordination systems cannot only be designed according to the established patterns (eq 1 and 2),[1] but also in the way described, e.g., for Scheme I. P^{III} containing systems are particularly suitable for this approach because one can take advantage of the acceptor function of a second row element substituent toward π systems, whereas at the same time it is possible to coordinate electrophiles to the basic P^{III} atom.

Acknowledgment. A fellowship of the Karl Winnacker Foundation is gratefully acknowledged (W.K.). We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Registry No. **1a**, 10498-57-4; **1b** Na$^+$, 87319-73-1; **2a** I$^-$, 87319-67-3; **2b**, 87319-74-2; **3a** 2I$^-$, 87319-68-4; **3b** I$^-$, 87319-75-3; **3b** Br$^-$, 87319-76-4; **4a**, 87319-69-5; **5a**, 87319-70-8; **6a**, 87319-71-9; **6b** Na$^+$, 59614-50-5; **7a**, 87319-72-0; **7b** I$^-$, 87319-79-7; **8a** 2I$^-$, 75841-72-4; **8a** 2Br$^-$, 10111-14-5; **8b** I$^-$, 87319-77-5; **8b** Br$^-$, 87319-78-6; **9a**, 77876-82-5; **10a**, 69220-11-7; **11a**, 77876-83-6; **12a**, 77876-84-7.

---

(24) Gerson, F.; Heinzer, J.; Bock, H.; Alt, H.; Seidl, H. *Helv. Chim. Acta* **1968**, *51*, 707.

(25) Cf.: Gerson, F. "High Resolution E.S.R. Spectroscopy"; Verlag Chemie: Weinheim, 1970.

(26) McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233.