Notes

Oxidation and Reduction of Phosphorus–Phosphorus and Arsenic–Arsenic Double Bonds. An Electrochemical Study of Two Diphosphenes and a Diarsene

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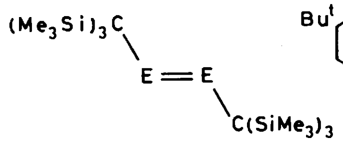
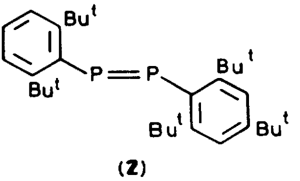
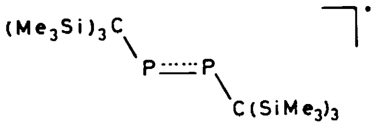
The diphosphenes $[(Me_3Si)_3C]_2P_2$ (**1**) and $(2,4,6\text{-}Bu^t_3C_6H_2)_2P_2$ (**2**) and the diarsene $[(Me_3Si)_3C]_2As_2$ (**3**) undergo electrochemical reduction in tetrahydrofuran (thf) solution to the corresponding anion radicals $[\{(Me_3Si)_3C\}_2P_2]^{\cdot-}$ (**4**), $[(2,4,6\text{-}Bu^t_3C_6H_2)_2P_2]^{\cdot-}$ (**5**), and $[\{(Me_3Si)_3C\}_2As_2]^{\cdot-}$ (**6**), respectively. Anion radicals (**4**) and (**5**) were sufficiently stable to permit the acquisition of e.s.r. data. The products of oxidation of (**1**), (**2**), and (**3**) were much more difficult to characterise. The oxidation of (**1**) in CH_2Cl_2 is irreversible at 25 °C; however, at −75 °C a one-electron oxidation occurs to the unstable cation radical $[\{(Me_3Si)_3C\}_2P_2]^{\cdot+}$. The oxidation of both (**2**) and (**3**) is irreversible even at −75 °C.

The results of theoretical studies on the model diphosphenes *trans*-HPPH [1] and *trans*-MePPMe [2] indicate the presence of a relatively low-lying lowest unoccupied molecular orbital possessing P=P π^* character. Accordingly, it was anticipated that facile reduction of diphosphenes (and heavier congeners) would occur, resulting in radical anions and possibly dianions *via* progressive population of the π^* orbital. Moreover, photoelectron spectroscopic studies [3,4a] and allied molecular orbital calculations on model diphosphene systems [1,2] reveal that electron ejection from the phosphorus lone pairs and/or P=P π bond should be feasible, thus raising the prospect of oxidation to cationic species, $[REER]^{n+}$ (E = P or As). The present study was initiated with a view to exploring the foregoing possibilities using electrochemical techniques and, where appropriate, e.s.r. spectroscopy. Prior electrochemical and e.s.r. work in this area is limited to preliminary reports [4,*] of the one-electron reduction of RP=PR (R = $2,4,6\text{-}Bu^t_3C_6H_2$).


E = P (**1**)
E = As (**3**)


(**2**)


(**4**)

Results and Discussion

Electrochemical and E.S.R. Experiments.—The reduction of $[(Me_3Si)_3C]_2P_2$ (**1**) [5] was studied by cyclic voltammetry (c.v.) in tetrahydrofuran (thf) solution at 25 °C in the presence of $[NBu^n_4][BF_4]$ as supporting electrolyte. A reversible reduction was apparent at −1.84 V *versus* s.c.e. (saturated calomel electrode). The peak separation is close to that anticipated for a Nernstian process (59 mV) and plots of i_p (peak current) *versus* $v^{\frac{1}{2}}$ (v = scan rate) are linear and the ratio of the cathodic to anodic peak currents is always one, thus indicating that the electron transfer is reversible and mass transfer is limited. The one-electron nature of the reduction was demonstrated by a bulk coulometry experiment which also resulted in the production of the purple anion radical (**4**). This anion radical is stable in thf solution for several days at room temperature thus permitting the acquisition of e.s.r. data. The principal feature of the e.s.r. spectrum of (**4**) (Figure) comprises a triplet [$a(^{31}P)$ = 43 G (G = 10^{-4} T), g = 2.018] thus suggesting that the single unpaired electron resides in the P=P π^* orbital which is delocalised over the diphosphorus centre. However, the central peak of the triplet exhibits a fine structure (a = 5 G) which is attributable to ^{29}Si hyperfine coupling. The ^{29}Si isotope ($I = \frac{1}{2}$) has a natural abundance of 4.7%, consequently in the six-silicon species, (**4**), the probability of one ^{29}Si being present is 22.2%. This calculated intensity agrees well with that observed for the satellites of the central peak.

A possible second one-electron reduction for (**1**) is observed at *ca.* 0.8 V more negative than that of the first reduction. However, it is difficult to be more definitive about this reduction because it occurs very close to the reduction potential of thf.

If the reduction of (**1**) is carried out in CH_2Cl_2 solution at 25 °C, the process is irreversible. The product(s) of this reaction have been neither isolated nor characterised. Interestingly, however, the rate of this side-reaction is sufficiently slow at −70 °C that the reduction becomes reversible.

The reduction of $(2,4,6\text{-}Bu^t_3C_6H_2)_2P_2$ (**2**) [6] occurs at −1.93 V *versus* s.c.e. The anion radical (**5**) is produced reversibly and

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[*] *Note added in proof*: Since the submission of this Note, a preliminary report has appeared on the electrochemical properties of (1) (M. Culcasi, G. Gronchi, J. Escudié, C. Couret, L. Pujol, and P. Tordo, *J. Am. Chem. Soc.*, 1986, **108**, 3130).

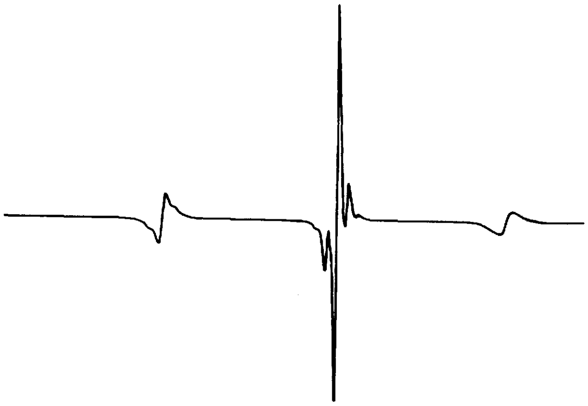
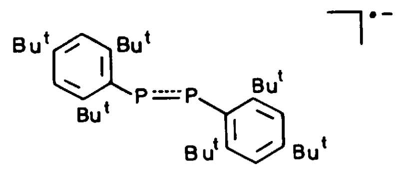
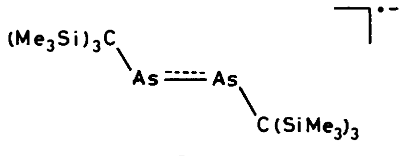


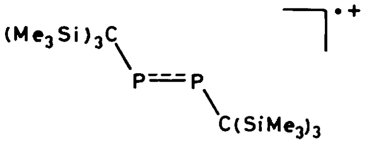
Figure. *X*-Band e.s.r. spectrum of $[\{(Me_3Si)_3C\}_2P_2]^{\bullet -}$ (4)



(5)



(6)



(7)

the wave-shape parameters are very similar to those for (**4**). Bulk electrolysis affords thf solutions of (**5**) which are stable for several days at 25 °C in the absence of air and moisture. The triplet appearance of the e.s.r. spectrum of (**5**) [$a(^{31}P) = 55$ G, $g = 2.013$] indicates that, as in the case of (**4**), it is likely that the unpaired electron occupies the P=P π^* orbital.

The one-electron reduction of $[(Me_3Si)_3C]_2As_2$ (**3**)[7] is also reversible on the time-scale of cyclic voltammetry and occurs at −1.3 V *versus* s.c.e. in thf–$[NBu^n_4][BF_4]$. Note that the reduction potential of the diarsene (**3**) is significantly less (~0.5 V) than that of the phosphorus analogue, (**1**). Along with the electronic spectral data,[8] this observation is consistent with the view that the π bond energy is less in diarsenes than in diphosphenes. The radical anion, (**6**), formed by bulk coulometry, is green in colour. However, it is distinctly less stable than the analogous phosphorus anion radicals and thf solutions of (**6**) decompose in a few minutes at room temperature. The lifetime of (**6**) can be prolonged by lowering the temperature; however, we were unable to record a satisfactory e.s.r. spectrum.

The oxidative processes for (**1**), (**2**), and (**3**) proved much more difficult to characterise. Oxidation of (**1**) in CH_2Cl_2 is completely irreversible at room temperature. However at −75 °C a reversible one-electron wave at +1.6 V *versus* s.c.e. is observed. Prolonged electrolysis at this potential produces a bright green solution which is stable at −75 °C but turns yellow as the solution is warmed to room temperature. It is presumed that the green compound which is formed is the radical cation (**7**); however, the thermal instability of this species precluded characterisation by e.s.r. spectroscopy. The oxidation of both (**2**) and (**3**) is completely irreversible even at −75 °C, and there is no indication of the presence of a radical cation analogous to (**7**).

Experimental

Starting Materials.—The diphosphenes, $[(Me_3Si)_3C]_2P_2$ (**1**)[5] and $(2,4,6\text{-}Bu^t_3C_6H_2)_2P_2$ (**2**),[6] and the diarsene $[(Me_3Si)_3C]_2As_2$ (**3**)[7] were prepared and purified according to literature methods.

E.S.R. Spectra.—*X*-Band e.s.r. spectra were measured on a Varian E9 instrument.

Electrochemical Experiments.—All electrochemical experiments were performed in a conventional three-electrode cell, using a Princeton Applied Research (PAR) model 173 potentiostat, a PAR model 175 universal programmer, a PAR model 179 digital coulometer, and a Houston Instruments model 2000 *X-Y* recorder. The voltammograms were obtained using a platinum disc electrode (area, 0.018 cm^2) whilst bulk electrolysis was carried out with a platinum gauze electrode (area, 10 cm^2). The surface of the platinum disc was checked for cleanliness by running cyclic voltammograms in 10 mol dm^{-3} H_2SO_4. Positive feedback was used to compensate for *iR* drop. The reference electrode was a silver wire (quasi-reference electrode). The silver wire was cleaned in an identical manner each time using dilute HNO_3 and deionised water. Ferrocene was added to the solution at the end of the experiment in order to reference the voltammetric waves to s.c.e. Two solvents were employed for the electrochemical measurements; thf and CH_2Cl_2. The thf was purified by distillation from Na–benzophenone under N_2 and the CH_2Cl_2 was purified by distillation from CaH_2 under N_2. The electrolyte, tetrabutylammonium tetrafluoroborate, was recrystallised twice from ethyl acetate–diethyl ether and vacuum dried at 140 °C (10^{-5} Torr, ~1.3×10^{-3} N m^{-2}). All solutions and cells were prepared and sealed inside a helium-filled Vacuum Atmospheres dry-box. Background voltammograms were run to verify the purity of the system.

Acknowledgements

We thank the National Science Foundation (U.S.A.) and the Robert A. Welch Foundation (U.S.A.) for generous financial support. We are also grateful to Gillian J. N. Thomas for running the e.s.r. spectra and Roger D. Moulton for insight into the electrochemical processes.

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Received 17*th December* 1985; *Paper* 5/2219