A comparison of the observed chemical shift with the calculated metal partial charge according to Sanderson[13] is presented in Figure 2. An increase in chemical shift with increasing partial positive charge is observed. The comparison here is more favorable than with ionic character as evidenced by the predicted lower binding energy for fluorides relative to chlorides which we have observed. The observed core electron binding energy trend in HgX_2 ($X^- = Cl^-$, Br^-, I^-) is also in agreement with the calculated charges on mercury in these compounds as estimated from measurement of the $5d^{10}$ ionization potential using uv photoelectron spectroscopy.[4]

Comparison of core electron binding energies for a series of halides with a common metal is not advisable since the same electron level has not been studied for each halogen and the extent of spin–orbit coupling for an identical electron level differs markedly in some cases. The trend in chemical shift for a common halogen with different metal ions is in partial agreement with the idea that more ionic compounds should exhibit larger halide chemical shifts. The calculated ionicities are in the order $Zn < Cd > Hg$. Only with the more highly covalent bromides and iodides do we find a discrepancy.

To obtain comparative data for mercury(I) salts the binding energies of selected mercury and chlorine energy levels were measured for Hg_2Cl_2 ($Hg\ 4f_{5/2,7/2}$, 103.7 ± 0.2, 99.4 ± 0.2; $Cl\ 2p_{1/2,3/2}$, 198.8 ± 0.2, 197.2 ± 0.2). The physical and chemical properties of Hg_2Cl_2 are consistent with the fact that the mercury–chlorine bond is predominantly ionic and that the ionicity is greater than that for the mercuric halides. In addition Scaife[14] has estimated that the ionicity of the Hg–Cl bond is about 79% in Hg_2Cl_2. Thus it might be expected that a significant shift in the binding energy of mercury would result. On the other hand it is known from spectroscopic studies[15] that mercurous mercury is $Hg_2{}^{2+}$, and a chemical shift indicative of the covalent mercury–mercury bond might result. That the latter result is in fact realized is noted by examining the chemical shifts for the mercury 4f levels. The chemical shifts for $Hg\ 4f_{7/2,5/2}$ of $+0.4$ and $+0.2$ eV, respectively, compare with a shift of about $+1.6$ eV for mercury in mercuric chloride. This result adds support to the notion that the dimeric mercurous mercury species, $Hg_2{}^{2+}$, is apparently characterized by strong covalent bonding although the mercury–chlorine bond is extremely ionic. That the Hg–Cl bond is more ionic than those noted in mercuric chloride is indicated by the greater negative chemical shift (greater electron density) for the chlorine $2p_{1/2,3/2}$ ($CS = -2.8$ eV for both levels) levels in Hg_2Cl_2. Thus the core binding energies for mercury and chlorine in mercurous mercury reinforce the conclusions from other studies which suggest that Hg_2Cl_2 be formulated as $Hg_2{}^{2+}$:$2Cl^-$.

Registry No. $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8; ZnI_2, 10139-47-6; CdF_2, 7790-79-6; $CdCl_2$, 10108-64-2; $CdBr_2$, 7789-42-6; CdI_2, 7790-80-9; HgF_2, 7783-39-3; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; Hg_2Cl_2, 10112-91-1.

(13) R. T. Sanderson, "Inorganic Chemistry," Reinhold, New York, N. Y., 1967.

(14) D. E. Scaife, *Aust. J. Chem.*, 24, 1753 (1971).

(15) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972.

Electrochemical Reduction of Phenylcyclopolyphosphines[1]

Timothy J. DuPont and Jerry L. Mills*

A great amount of work on the alkali metal reduction of phenylcyclopolyphosphines has been done, largely by Issleib and coworkers.[2] However, most of the experiments were performed when it was believed that phenylcyclopolyphosphine was a tetrameric species, $(C_6H_5P)_4$. It is now known from X-ray crystallographic work that the so-called "A" and "B" forms are pentameric[3] and hexameric,[4] respectively, although it is still not clear whether these species are different in solution.[5] In order to clarify the confusion concerning the solution structures of these compounds, and also to reexamine their reduction under carefully controlled conditions, the results of an electrochemical investigation of pentaphenylcyclopentaphosphine (A) and hexaphenylcyclohexaphosphine (B) are reported. The only known cyclic trimeric phosphine,[2d,6] $K_2(C_6H_5P)_3$, which is formed by potassium reduction of pentaphenylcyclopentaphosphine, was also reexamined.

Experimental Section

Instrumental. Electrochemical experiments were made using a Wenking Model 66TS10 potentiostat and a Chemtrix Type 800-A waveform generator in conjunction with a Plotamatic Model 715 x-y recorder or, for fast techniques, a Tektronix Type 564B storage oscilloscope. Some measurements were also performed on a Princeton Applied Research Corp. (PAR) electrochemical system, Model 170. A Varian Associates nmr spectrometer Model XL-100-15 was used for ^{31}P spectra. Proton nmr spectra were run on the same instrument or on a Varian A-60. Raman spectra were recorded on a Jarrell-Ash Model 25-500 laser Raman, and ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Uv–visible spectra were obtained on a Cary 17 spectrophotometer.

Preparations. (a) Pentaphenylcyclopentaphosphine, $(C_6H_5P)_5$. Pentaphenylcyclopentaphosphine[9] was prepared by dropwise addition of 8.95 g (0.05 mol) of dichlorophenylphosphine to 1.22 g (0.05 mol) of magnesium turnings in 50 ml of tetrahydrofuran (THF). After complete addition of the phosphine, 60 ml of H_2O was added to form a two-phase system with the resultant precipitation of the pentamer in the organic layer. Recrystallization from THF yielded crystals melting at 149–150°. A Raman spectrum run of the solid in a sealed glass tube agreed well with that previously reported,[10] as did a Nujol mull ir spectrum.[9] A uv spectrum run under anaerobic conditions in THF exhibited peaks at 323, 293, and 241 nm. A ^{31}P nmr spectrum in THF exhibited a single resonance at $+4.0$ ppm (relative to 85% H_3PO_4), and a proton nmr spectrum[9] in CS_2 exhibited absorptions at 7.05, 7.19, 7.13, and 7.25 ppm (relative to TMS) in order of

(1) Presented in part before the Inorganic Division, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

(2) (a) V. E. Fluck and K. Issleib, *Z. Anorg. Allg. Chem.*, 339, 274 (1965); (b) K. Issleib and K. Krech, *Chem. Ber.*, 99, 1310 (1966); (c) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, 22, 385 (1957); (d) K. Issleib and E. Fluck, *Angew. Chem., Int. Ed. Engl.*, 5, 587 (1966); (e) K. Issleib and K. Krech, *Chem. Ber.*, 98, 2545 (1965).

(3) J. J. Daly, *J. Chem. Soc.*, 6147 (1964); J. J. Daly and L. Maier, *Nature (London)*, 203, 1167 (1964).

(4) J. J. Daly and L. Maier, *Nature (London)*, 208, 383 (1965).

(5) A. H. Cowley, *Top. Phosphorus Chem.*, 5, 1 (1967).

(6) A previously reported trimer[7] $[(C_2F_5)_3P]_3$, has since been shown to be a mixture of tetramer and pentamer.[8]

(7) A. H. Cowley, T. A. Furtsch, and D. S. Dierdorf, *Chem. Commun.*, 523 (1970).

(8) P. S. Elmes, M. E. Redwood, and B. O. West, *Chem. Commun.*, 1120 (1970).

(9) W. A. Henderson, Jr., M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 85, 2462 (1963).

(10) R. L. Amster, W. A. Henderson, and H. B. Colthur, *Can. J. Chem.*, 42, 2577 (1964).

decreasing intensity and a broad band at 7.72 ppm. Care was taken in all solution measurements to exclude oxygen and water.

(b) **Hexaphenylcyclohexaphosphine,**[9] **$(C_6H_5P)_6$.** Hexaphenylcyclohexaphosphine was prepared by adding, all at once, 5.90 g (33 mmol) of dichlorophenylphosphine to 3.63 g (33 mmol) of phenylphosphine in 15 ml of benzene. After evolution of HCl, the precipitate which formed was recrystallized from 50 ml of THF. The product obtained was dried *in vacuo* and gave a melting point of 197–201° in an evacuated capillary tube. Raman[10] and ir spectra[9] corresponded to the literature. A uv spectrum in THF exhibited absorptions at 320, 297, and 245 nm. A ^{31}P nmr spectrum was run in THF in a sealed tube at 80° (due to low solubility), and a single resonance was observed at 4.0 ppm. Upon cooling, the hexamer was reprecipitated and identified by its ir spectrum and melting point. Proton absorptions[9] in CS_2 appeared at 7.06, 7.02, 6.96, and 6.92 ppm (relative to TMS) in order of decreasing intensity, with a broad band at 7.35 ppm.

(c) **Potassium Triphenylcyclotriphosphine,**[2d] **$K_2(C_6H_5P)_3$.** Potassium triphenylcyclotriphosphine was made by refluxing 0.18 g (4.6 mmol) of K with 0.76 g (1.4 mmol) of the pentamer in 150 ml of THF for 1 hr. The compound exhibited a singlet in the ^{31}P nmr spectrum at +49.8 ppm. The analogous sodium salt was prepared in a similar fashion.

(d) **Hexaphenylcyclohexaarsine, $(C_6H_5As)_6$,** was prepared according to the method of Holliman and Mann[11] using 0.48 g (21 mmol) of sodium metal and 2.23 g (10 mmol) of $C_6H_5AsCl_2$. The melting point in a sealed capillary was 210–213°. The ir spectrum agreed with the literature.[12] The Raman spectrum of the solid taken in a sealed capillary exhibited peaks at 172 (sh), 182 (vs), 190 (sh), 210 (m), 220 (m), 260 (s), 275 (s), 296 (m), 316 (m), 616 (w), 997 (vs), and 1021 cm^{-1} (m).

Electrochemical Measurements. The cell used was of a three-electrode configuration and was vacuum tight allowing for rigorous exclusion of oxygen and water. Routine preparation and operation of the cell have been previously described.[13] Polarograms were run using a 6–12-sec drop capillary while cyclic voltammograms utilized a platinum bead. Unless otherwise specified, $E_{p/2}$ valves for cyclic voltammograms are reported for sweep rates of 250 mV/sec. Controlled-potential coulometry was done at a mercury pool with a copper wire auxiliary electrode, sealed from the working solution by a glass frit. In all cases THF (Baker, spectroscopic grade), purified as previously described,[13] was used as the electrochemical solvent, and tetrabutylammonium perchlorate (TBAP) (Southwestern Analytical) was the supporting electrolyte. The Ag wire|0.1 M Ag$^+$ (THF) reference electrode was measured to be +0.49 V *vs.* sce. All potentials reported, however, are *vs.* the Ag|Ag$^+$ electrode. Visible spectra for electrochemically generated degradation species were obtained by exhaustive reduction of THF solutions of the pentamer or hexamer in a platinum two-electrode cell, similar to one which has been previously described.[14] Uv–visible spectra of solutions of the reduced pentamer, reduced hexamer, $K_2(C_6H_5P)_3$, and $Na_2(C_6H_5P)_3$ exhibited broad featureless absorptions beginning at 500 nm and gradually increasing to the uv cutoff.

Results and Discussion

The reduction of $(C_6H_5P)_5$ at a dropping mercury electrode in THF exhibited a wave with $E_{1/2} = -2.62$ V *vs.* Ag|Ag$^+$. A plot of log $[i/(i_d - i)]$ *vs.* V yielded a slope of 63 mV. Since controlled-potential coulometry at -3.1 V showed a two-electron reduction, the value of 63 mV indicates non-nernstian behavior. Cyclic voltammetry at a platinum bead (see Figure 1A) showed the reduction to be totally chemically irreversible at sweep rates varying from 250 mV/sec to 12.5 V/sec. The cyclic voltammetric reduction wave with $E_{p/2} = -2.8$ V was coupled to three anodic waves $E_{p/2} = -1.0$ (very small), -1.4, and -1.9 V, with the -1.9 V wave being particularly favored by rapid scan rates. Therefore, the relative intensity of the waves was dependent upon scan rates. Controlled-potential electrolysis followed by cyclic voltammetry (see Figure 1B) at a platinum bead indicated that a reducible species ($E_{p/2} = -2.8$ V) not originally present in the elec-
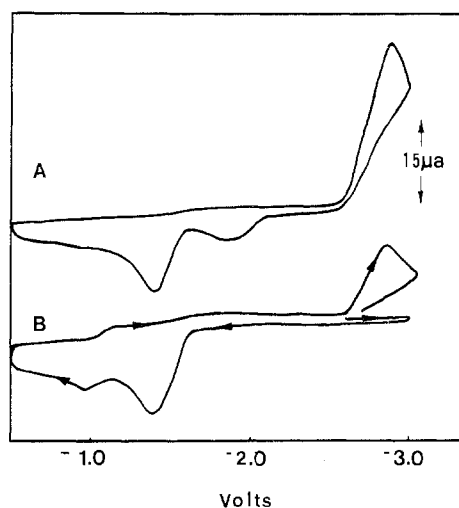
(11) F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 30 (1945).
(12) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Aust. J. Chem.*, **16**, 285 (1963).
(13) J. L. Mills, R. Nelson, S. G. Shore, and L. B. Anderson, *Anal. Chem.*, **43**, 157 (1971).
(14) G. Glass and R. West, *Inorg. Chem.*, **11**, 2847 (1972).

Figure 1. Cyclic voltammograms at a platinum bead electrode (scan rate, 250 mV/sec): A, pentaphenylcyclopentaphosphine (initial potential, -0.5 V); B, pentaphenylcyclopentaphosphine after exhaustive electrolysis (initial potential, -2.6 V).

trolyzed solution was formed after scanning through the two anodic waves ($E_{p/2} = -1.0$ and -1.4 V). The reducible species was coupled primarily, if not completely, to the wave at -1.4 V.

The electrochemical behavior of $(C_6H_5P)_6$ was very similar to that of the pentamer. The polarogram exhibited a reduction wave at $E_{1/2} = -2.62$ V, shown by controlled-potential coulometry to involve two electrons. The wave was non-nernstian with a plot of log $[i/(i_d - i)]$ *vs.* V yielding a slope of 62 mV. Cyclic voltammograms (see Figure 2) showed a reduction wave with $E_{p/2} = -2.8$ V coupled to three anodic peaks at -1.0, -1.4, and -1.9 V. As in the case of the pentamer, the relative intensity of the three anodic waves was very dependent on scan rate. The anodic behavior of the reduced hexamer was considerably different, however, from the anodic behavior of the reduced pentamer. In general, the wave at -1.0 V was relatively more prevalent in the hexamer and the wave at -2.0 V was more prevalent in the pentamer. Cyclic voltammograms and uv–visible spectra (see Experimental Section) run on electrolyzed solutions of the hexamer were identical with those of the electrolyzed pentamer.

The electrochemical reduction at either a dme or a platinum bead electrode of both the pentamer (form A) and hexamer (form B) is consistent with a simultaneous non-nernstian two-electron transfer to the rings followed by very rapid ring degradation.

$$(C_6H_5P)_n \xrightarrow{2e} [(C_6H_5P)_n{}^{2-}] \xrightarrow{fast} \text{ring degradation products}$$
$$n = 5 \text{ or } 6$$
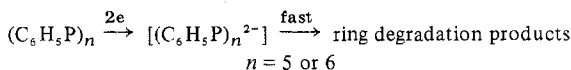
The anodic waves result from the oxidation of anionic ring degradation products (*vide infra*). This behavior is analogous to the alkali metal reductions previously reported,[2] where the composition of the ring degradation products, M_2-$(C_6H_5P)_n$ (M = alkali metal, $n = 1$–5), depends upon the reaction stoichiometry. With the chemical reduction, apparently as many as two electrons per C_6H_5P moiety can be transferred, but in the electrochemical reduction, only two electrons per ring can be transferred. Even though the solutions of $(C_6H_5P)_5$ and $(C_6H_5P)_6$ are virtually indistinguishable electrochemically, it is clear, particularly from uv–visible, ^1H nmr, and solution ir data[9] (see Experimental Section),
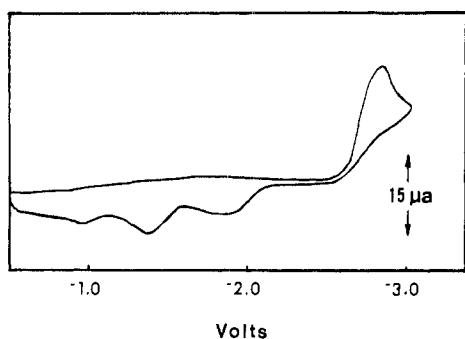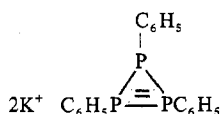
Figure 2. Cyclic voltammogram of hexaphenylcyclohexaphosphine (scan rate, 250 mV/sec; initial potential, −0.5 V).

that the pentamer and hexamer are distinct species in solution.

The compound $K_2(C_6H_5P)_3$ has been reported[2d] to be of the structure

$$2K^+ \quad C_6H_5P\overset{\overset{\displaystyle C_6H_5}{\displaystyle |}}{\overset{\displaystyle P}{\underset{\triangle}{{=}}}}PC_6H_5$$

based largely on the singlet at +49.8 ppm in the ^{31}P nmr spectrum. A cyclic voltammogram of a THF solution was indistinguishable from the cyclic voltammograms of the electrolyzed $(C_6H_5P)_5$ or $(C_6H_5P)_6$ solutions. Also indistinguishable were the uv-visible spectra. Additionally, sodium reduction products of the stoichiometry $Na_2(C_6H_5P)_3$ exhibited the same anodic wave at −1.4 V and the same coupled cathodic wave.

These data are consistent with the anodic wave at −1.4 V representing oxidation of a *linear* trimeric species, $(C_6H_5P)_3^{2-}$, in all of the solutions, whether chemically or electrochemically reduced. As reported previously,[2b] the sodium compound, $Na_2(C_6H_5P)_3$, does not exhibit a single ^{31}P resonance, thus negating the possibility of a trimeric ring structure in this compound, consistent with the argument[2d] that only potassium of the alkali metals was able to stabilize a three-membered ring. However, considering that all of the reduced solutions, whether from chemical or electrochemical origin, exhibit the same electrochemical behavior, it appears the only special feature of $K_2(C_6H_5P)_3$ is that it is undergoing rapid exchange on the nmr time scale. Experiments performed on a wide range of reaction stoichiometries never yielded more than a single ^{31}P resonance. In many cases no resonance was observable at room temperature,[15] suggesting intermediate exchange rates and lending credence to the exchange hypothesis.

Oxidation of the linear trimer, $(C_6H_5P)_3^{2-}$, apparently leads to reformation of the five- or six-membered ring (see Figure 1B). This recoupling phenomenon also occurs upon hydrolysis of the chemically reduced species,[2d] producing $C_6H_5PH_2$ as well as $(C_6H_5P)_5$. Inasmuch as the mechanism for the recoupling is not known and is undoubtedly very complex,

(15) Limited solubility precluded low-temperature nmr studies.

no kinetic data were taken. The anodic waves at −1.0 and −2.0 V cannot be unequivocally assigned; however, the data are consistent with the assignment of the wave at −2.0 V to a monomeric species $(C_6H_5P)^{2-}$. For example, the anodic sweep of cyclic voltammograms run on a THF solution of the stoichiometry $K_2(C_6H_5P)$ exhibited the principal wave at −2.0 V. The presence of the −2.0 V wave prevents recoupling of the trimer wave. Also the monomer wave is initially evident on cyclic voltammograms run on the partially electrolyzed solutions of $(C_6H_5P)_5$ or $(C_6H_5P)_6$. However, if the electrolysis is discontinued, and the solution stirred for several minutes, the monomer wave slowly disappears, indicating slow redistribution reactions occurring among the reduced species. Apparently the monomer is a transient species formed as one of the principal electrochemical reduction degradation products of either $(C_6H_5P)_5$ or $(C_6H_5P)_6$, with it being relatively a more important product in the case of the former. Rapid scan rates, therefore, accentuate its presence. The anodic wave at −1.0 V is consonant with a dimeric species, but this must be viewed as a very tentative assignment. The −1.0 V wave is small during cyclic voltammetric sweeps (Figures 1A and 2), particularly in the case of $(C_6H_5P)_5$, and is therefore apparently not an important primary ring degradation product. The wave grows, however, as there is time for slow chemical redistribution reactions to occur, as after partial or complete coulometry (Figure 1B). Neutral ring fragments, such as $C_6H_5PH_2$,[16] formed, for example, by proton abstraction from the solvent, are electroinactive.

Preliminary experiments on $(C_6H_5As)_6$ indicate that its electrochemical behavior is similar to that of its phosphorus congener. Originally a single reduction wave appears at $E_{p/2}$ = −2.8 V in a cyclic voltammogram followed by anodic waves which appear after partial coulometry at −1.2, −1.5, and −2.0 V. After exhaustive coulometry, recoupling occurs following oxidation of the anodic waves. An accurate determination of the n value, the number of electrons involved in the reduction, is difficult to ascertain, however, because of a second reducible species which is formed during the coulometry. This wave occurs at $E_{p/2}$ = −3.0 V and probably belongs to a neutral diarsine, which, as has been reported,[16] may be electroactive, unlike the diphosphines.

Further electrochemical studies are being performed on other cyclopolyphosphines, particularly with the hope of elucidating the complex redistribution and recoupling reactions which occur with the reduced species.

(16) R. E. Dessy, T. Chivers, and W. Kitching, *J. Amer. Chem. Soc.*, **88**, 467 (1966).