H, 5.86; N, 21.73. *N*-Nitroso-*N*-(*p*-methoxybenzyl)urea (**4e**): mp 118–120 °C. Anal. Calcd for $C_9H_{11}N_3O_3$: C, 51.67; H, 5.30; N, 20.09. Found: C, 51.71; H, 5.39; N, 20.11.

Kinetics of Solvolysis of *N*-Nitroso-*N*-(*p*-Y-benzyl)ureas. An aliquot (30 μL) from an appropriately concentrated stock solution of the individual *N*-nitroso-*N*-(*p*-Y-benzyl)urea dissolved in ethanol was added to 3 mL of aqueous 0.1 M phosphate buffer (pH 6.9) 40 °C to arrive at final concentrations of the nitroso compound in the range of 10^{-4} M. Rates of disappearance of the *N*-nitroso-*N*-(*p*-Y-benzyl)ureas were determined from the time-dependent decrease in absorbance of these solutions at 235 nm. Observed first-order rate constants (k_{obsd}) were calculated from the slopes of plots of ln ($OD_t - OD_\infty$) vs. time, and the reported k_{obsd} values are the average of three determinations. Values of k_{obsd} (min^{-1}) for the *N*-nitroso-*N*-(*p*-Y-benzyl)ureas (**4a–e**) under these conditions are as follows: **4a**, 22.7 × 10^{-2}; **4b**, 13.4 × 10^{-2}; **4c**, 9.93 × 10^{-2}; **4d**, 9.07 × 10^{-2}; **4e**, 9.32 × 10^{-2}.

Aralkylation of [5′-^{3}H]Guanosine. An aliquot (10 μL) from an aqueous stock solution of [5′-^{3}H]guanosine (**1**) (1 × 10^{-5} M) was added to 1 mL of 0.1 M phosphate buffer, pH 6.9, 40 °C. An aliquot (10 μL) from a freshly prepared stock solution of the *p*-Y-benzyl halide (**2a–e** or **3a–e**) in DMF was added to achieve final reaction solutions which were 1.7 × 10^{-2} M in aralkyl halide. The appropriate amount of *N*-nitroso-*N*-(*p*-Y-benzyl)urea (**4a–e**) was added as a solid. The resulting suspensions were incubated at 40 °C with constant stirring until reactions were complete, at which time the appropriate mixture of marker nucleosides in methanol was added and the product mixtures were loaded on a 0.78 × 30 cm Aminex A-5 (Bio-Rad Laboratories, Richmond, CA) column. Elution with acidic ammonium formate solutions was as previously described.[18,20] Imidazole-ring-opened products derived from the 7-substituted guanosines (**5a–e**) elute after guanosine during elution with the first 100 mL of buffered solvent.[20] Because O^6-(*p*-methylbenzyl)guanosine (**7d**) decomposes under the acidic column conditions,[20] product mixtures derived from reactions of guanosine with **2d–4d** were first loaded on the Aminex A-5 column equilibrated with 1 M $NH_4^+HCO_2^-$, pH 9.3, 45 °C. UV absorption was continuously monitored at 254 nm and fractions (1 mL) were collected and mixed with 10 mL of PCS (Amersham/Searle) for scintillation counting. Unmodified guanosine elutes in fractions 17–21 under these conditions. When 60 mL of this solvent had passed through the column, elution was carried out with 0.85 M $NH_4^+HCO_2^-$ in DMF/H_2O (12:88), pH 9.3, 45 °C. N^2-(*p*-Methylbenzyl)guanosine (**6d**) elutes in fractions 100–110, O^6-(*p*-methylbenzyl)guanosine (**7d**) elutes in fractions 120–130, and 4-(*p*-methylbenzyl)-5-guanidino-1-β-D-ribofuranosylimidazole (**8d**) elutes in fractions 150–160. The amount of 7-substituted guanosine (**5d**) produced in these reactions was quantified by eluting the column with the acidic buffers described previously.[20]

A tabular summary of the percent yield for products **5–8** is presented in Table I.

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Electrochemical Reduction of Trivalent Organophosphorus Compounds: Mechanism and Products from Phosphorus–Heteroatom Bond Cleavage

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The cathodic cleavage at platinum electrodes of phosphorus–heteroatom bonds in fluoro-, chloro-, and bromodiphenylphosphine and in phenyl diphenylphosphinite in dry acetonitrile solution has been accomplished with the formation of tetraphenyldiphosphine as the exclusive product. A mechanism that involves the intermediacy of diphenylphosphinyl anions is suggested on the basis of cyclic voltammetry and controlled potential coulometry studies.

Introduction

The application of electrochemical techniques to the synthesis of organic compounds is an area which is rapidly developing. Relatively little attention, however, has been devoted to the study of organophosphorus compounds. We have undertaken an investigation of the electrochemical cleavage of phosphorus–heteroatom bonds in trivalent phosphorus compounds in anticipation that either the radicals II or the anions III (eq 1) which are potential intermediates might be synthetically useful.

$$Ph_2PX + e^- \rightarrow Ph_2PX^{\bullet -} \rightarrow \underset{\text{II}}{Ph_2P^\bullet} + X^- \xrightarrow{e^-} \underset{\text{III}}{Ph_2P^-} \qquad (1)$$

Ia, X = Cl
Ib, X = Br
Ic, X = F
Id, X = OPh

Dessy et al.[1] have reported that reduction of chlorodiphenylphosphine, Ia, at a mercury cathode at −3.4 V vs. Ag|$AgClO_4$ in glyme resulted in the formation of diphenylphosphine (eq 2). Dessy interpreted this to result

$$Ph_2PCl + e^- \rightarrow Ph_2P^\bullet + Cl^- \xrightarrow{\text{S-H}} Ph_2PH \qquad (2)$$

from a one-electron reduction forming the diphenylphosphinyl radical, II, which subsequently abstracted hydrogen from the solvent forming product (eq 2). These authors reported that no reversibility was detected by cyclic voltammetry using sweep rates of up to 100 V/s.

Results

We have investigated the cyclic voltammetry of Ia–d at a platinum disk electrode in painstakingly dried acetonitrile containing tetra-*n*-butylammonium perchlorate as an electrolyte. We have observed rather complex concentration and sweep rate dependent behavior, and the peaks observed are broad and poorly defined. Additional scouting studies of the cyclic voltammograms at glassy carbon and at mercury gave completely analogous results, and the results obtained were identical with and without use of *iR* compensation. Figure 1 shows cyclic voltam-

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(1) Dessy, R. E.; Kitching, W. *J. Am. Chem. Soc.* **1966**, *88*, 467.

Table I. Cyclic Voltammetric Data for Ia–d

concn	$E_p{}^a$ $(i)^b$			
	R_1	R_2	O_1	O_2
		Ia		
0.0067^c	–0.97 (50)	–2.94	–2.80	–0.63
0.0134^c	–1.38 (85)	–2.96	–2.76	–0.60
0.0268^c	–1.41 (155)	–3.04	–2.82	–0.64
0.0534^c	–1.47 (250)	–2.90	–2.87	–0.66
0.0067^d	–1.02 (70)	–2.97	–2.78	–0.64
0.0134^d	–1.50 (120)	–2.98	–2.78	–0.61
0.0268^d	–1.56 (220)	–3.10	–2.80	–0.65
0.0534^d	–1.45 (355)	–2.91	–2.54	–0.67
0.0067^e	–1.13 (110)	–3.00	–2.76	–0.63
0.0134^e	–1.60 (185)	–3.00	–2.78	–0.57
0.0268^e	–1.88 (325)	–3.15	–2.77	–0.66
0.0534^e	–1.87 (550)	–3.09	–2.52	–0.65
		Ib		
0.0067^c	–0.87 (60)	–2.94	–2.54	–0.68
0.0134^c	–1.02 (90)	–2.95	–2.82	–0.66
0.0268^c	–1.50 (180)	–2.76	–2.58	...
0.0134^d	–1.32 (125)	–2.97	–2.77	...
0.0268^d	–1.56 (245)	–2.79	–2.56	0.63
0.0134^e	–1.42 (195)	–3.00	–2.74	–0.66
0.0268^e	–1.68 (380)	–2.87	–2.57	–0.66
		Ic		
0.0067^c	–1.64 (40)	–2.84	–2.70	–0.66
0.0134^c	–1.80 (45)	–2.88	–2.69	–0.63
0.0067^d	–1.80 (55)	–2.85	–2.71	–0.66
0.0134^d	–2.07 (65)	–2.90	–2.69	–0.69
0.0067^e	–1.98 (80)	–2.88	–2.66	–0.63
0.0134^e	–2.32 (100)	–2.93	–2.66	–0.66
		Id		
0.0150^c	–1.80 (15)	–2.88	–2.61	...
0.0300^c	–2.26 (100)	–3.00	–2.73	–0.63
0.0150^d	–2.14 (22)	–2.89	–2.61	–0.60
0.0300^d	–2.34 (140)	–3.00	–2.72	–0.61
0.0150^e	–2.40 (40)	–2.94	–2.68	...
0.0300^e	–2.47 (220)	–3.05	–2.73	–0.57

[a] V vs. Ag/Ag^+. [b] μ, A. [c] 100 mV/s. [d] 200 mV/s. [e] 500 mV/s.

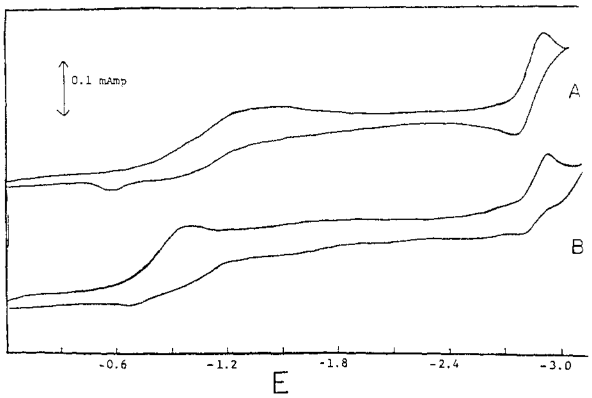

Figure 1. Cyclic voltammograms. A: compound Ia; B: compound Ib (concentration 0.0134 M in acetonitrile containing 0.1 M tetra-*n*-butylammonium bromide; sweep rate 200 mV/s; reference electrode Ag|$AgNO_3$).

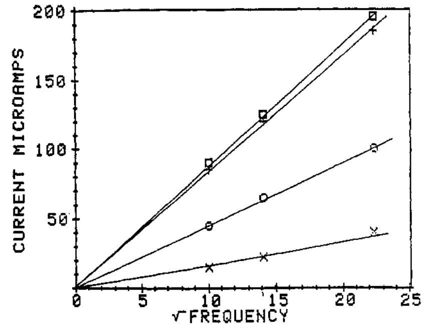

Figure 2. Dependence of cyclic voltammetric current on the square root of sweep frequency for compounds Ia–d: +, Ia (0.0134 M); □, Ib (0.0134 M); ○, Ic (0.0134 M); ×, Id (0.015 M).

mograms of Ia and Ib at platinum. At the lowest concentration investigated, 6.7 mM, and at scan rates of 100 mV/s both Ia and Ib exhibited two reduction waves. In the case of Ia these included a broad peak at –0.95 V (vs. Ag|Ag^+) and another at –2.92 V. The first wave was not reversible through the highest scan rates investigated, 500 mV/s. The second wave was quasi-reversible with the anodic E_p at –2.79 V. A small second oxidation peak was observed at –0.63 V. Completely analogous behavior was observed for Ib, Ic, and Id under identical conditions. Peak potentials for all four compounds are tabulated in Table I. At higher concentrations the first cathodic peak moved to more negative potential and broadened dramatically. For Ia at 100 mV/s the peak maxima occurred at –0.97, –1.38, –1.41, and –1.47 V at concentrations of 0.0067, 0.0134, 0.0268, and 0.0534 M, respectively. This peak also moved to more negative potential with increasing scan rate and plots of i_p vs. the square root of the sweep frequency are linear over the entire range of concentrations studied. Figure 2 illustrates this relationship for compounds Ia–D. The peak current also varied as a function of the concentration, but not linearly. Figure 3 illustrates this behavior for compound Ia; similar behavior was observed for the other compounds. At the higher concentrations the current was lower than would have been predicted if a linear dependence was obeyed.

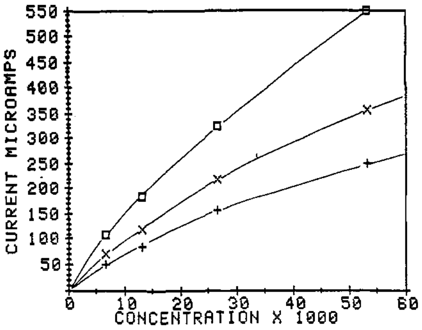

Figure 3. Dependence of cyclic voltammetric current on concentration of compound Ia: +, 100 mV/s; ×, 200 mV/s; □, 500 mV/s.

The observed E_p's for the first reduction in each compound were observed to shift to more negative potential as the leaving group was varied from Br to Cl to F to phenoxy.

All four compounds exhibited a second reduction peak which was quasi-revesible, and within the limits of experimental error these peaks occurred at the same potential. A complete tabulation of these data can be found in Table I.

Compounds Ia and Ib also exhibited another interesting oxidation peak. If a normal scan starting at 0.0 V was stopped at −1.6 V and held at this potential for a period of time and then reversed, an intense peak was observed at −1.0 V. On a subsequent normal cycle (0.0 to −3.0 V and then reversing) this peak either was very small or was not observed. The current of an oxidation peak at −0.63 V was however enhanced under these conditions.

A controlled potential electrolysis at −1.6 V (vs. Ag|Ag$^+$) was performed with 0.004 mol of Ia in 200 mL of dry acetonitrile, containing tetra-*n*-butylammonium bromide (0.1 M) as electrolyte, at a monel electrode in a flow cell with a microporous glass separator. The current dropped below the original background current after passage of 396 coulombs which corresponds to a one-electron reduction. A single product was obtained on workup of the solution and was identified by comparison of gas chromatographic retention times with those of a commercial sample and by ^{31}P NMR as tetraphenyldiphosphine. Gas chromatographic analysis indicated that a 92% yield of product was obtained. The cyclic voltammogram of this product exhibited a quasi-reversible peak at approximately −2.9 V, and a weak oxidation wave at −0.63 V was also observed. These peaks correspond to those observed in the cyclic voltammograms of Ia–d.

Discussion

These data are interpreted to arise from the reaction processes shown in eq 3–5. Equation 3 illustrates the

$$\mathrm{Ph_2PX} + e^- \rightarrow \mathrm{Ph_2PX}^{\bullet-} \rightarrow \underset{\mathrm{II}}{\mathrm{Ph_2P}^{\bullet}} + \mathrm{X}^- \tag{3}$$

$$\mathrm{Ph_2P}^{\bullet} + e^- \rightarrow \underset{\mathrm{III}}{\mathrm{Ph_2P}^-} \tag{4}$$

$$\mathrm{Ph_2P}^- + \mathrm{Ph_2PX} \rightarrow \underset{\mathrm{IV}}{\mathrm{Ph_2P{-}P_2Ph}} + \mathrm{X}^- \tag{5}$$

process resulting from the first reduction wave which occurs at −0.97 and −0.87 V for Ia and Ib, respectively, at 6.7 mM, and at a sweep frequency of 100 mV/s. The reaction is not reversible because of the rapid, or simultaneous, cleavage of the phoshorus–halogen bond, yielding the diphenylphosphinyl radical, II. EC type reactions in which the following chemical reaction is fast are characterized by cyclic voltammograms in which a plot of i_p vs. the square root of the sweep frequency is linear[2] and in which the E_p's observed shift to more negative potential with increasing sweep frequency.[3] All four compounds exhibit this behavior (see Figure 2 and Table I). It is interesting to note that the slopes of these plots increase with increasing leaving group ability of the substituent X, i.e., Br > Cl > F > OPh.[4] It would be expected that the greater the rate of the subsequent cleavage reaction the greater influence a faster scan rate would have on the observed current.

These observations do exclude another plausible mechanism[5] which is shown in eq 6 and 7. A chemical step (eq

$$2\mathrm{Ph_2PCl} \rightarrow \mathrm{Ph_2(Cl)P^+{-}PPh_2} + \mathrm{Cl}^- \tag{6}$$

$$\mathrm{Ph_2(Cl)P^+{-}PPh_2} + e^- \rightarrow \mathrm{Ph_2(Cl)\dot{P}{-}PPh_2} \xrightarrow{e^-} \mathrm{Ph_2P{-}PPh_2} + \mathrm{Cl}^- \tag{7}$$

6) preceding the electrochemical reaction, i.e., a CE mechanism, results in cyclic voltammograms in which E_p shifts anodically with an increase in sweep frequency,[6] which is not in accord with our observations (Table I).

Equation 4 proposes the reduction of the phosphinyl radical to the corresponding anion. If this reduction takes place at a potential positive or at approximately the same as that of the first reduction, a second reduction wave will not be observed. This has been observed in the possibly analogous carbon system.[7] The appearance of the large transient oxiidation wave at −1.0 V which is observed to grow when the potential scan is stopped and maintained at −1.6 V before rapidly scanning anodically can be attributed to the oxidation of the anion back to the corresponding radical, i.e.,the reverse of eq 4. This peak is not observed in a normal cyclic voltammogram, presumably because of the very short lifetime of the anion intermediate (vide infra).

Another possible mechanism for the formation of the phosphinyl anion would be a two-electron transfer which could result in the formation of the anion without involving the intermediacy of the radical. Our data cannot distinguish between these possibilities.

Equation 5 proposes that the diphosphine product could arise from attack of III on the starting material; this does indeed occur in the alkali-metal-induced synthesis of the biphosphine from Ia.[8] The cyclic voltammetry data also support formation of product in this manner. Figure 3 illustrates the relationship between current and concentration for the first reduction wave. An increase in concentration does not result in the increase in current that would be expected on the basis of a linear relationship. This is consistent with a mechanism in which a single diffusion process decreases the starting material by more than one molecule. Equations 3 through 5 are compatible with this expectation, since the phosphinyl anion which is formed reacts with a second molecule of starting ma-

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(2) Bond, A. M. *Modern Polarographic Methods in Analytical Chemistry*; Marcel Dekker: New York, 1980; p 195.

(3) Reference 2, p 195.

(4) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 331.

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terial, thus decreasing the concentration gradient of starting material reaching the electrode surface. Our coulometry measurements are in accord with a one electron per molecule consumption of starting material or two-electron transfer per molecule of product formed.

The observations discussed above argue against another possible mechanism for the formation of the dimer product. The formation of phosphinyl radicals (eq 3) and their subsequent dimerization (eq 8) could account for the

$$2Ph_2P^{\bullet} \rightarrow Ph_2P\text{–}PPh_2 \qquad (8)$$

formation[9] of compound IV and is in accord with our observed coulometry. We would expect that this process would require a linear relationship between current and concentration since both radicals would have to be formed from diffusion to the electrode surface. We also were not able to detect any trapping products when cyclohexene was included in the reaction mixture.

The quasi-reversible reduction peak observed in the cyclic voltammograms of all four compounds at approximately −2.96 V also appears in the cyclic voltammogram of IV and thus may be assigned to the reactions shown in eq 9.

$$Ph_2P\text{–}PPh_2 + e^- \rightleftarrows Ph_2P\text{–}PPh_2^{\bullet -} \qquad (9)$$

The small anodic wave observed at −0.63 V is also observed in the cyclic voltammogram of IV as a small peak. We observe a much larger peak at this potential in the cyclic voltammogram of diphenylphosphinic acid, Ph_2PO_2H. We thus attribute this oxidation process to result from impurities or from products resulting from the reaction of adventitious oxygen with either our starting material or intermediates formed in the reduction process. The oxidation of some substituted derivatives of tetraphenyldiphosphine to the corresponding radical cations have recently been reported[10] to occur at approximately +0.6 V.

We have attempted to trap the anionic intermediate in this reaction without success. The inclusion of a tenfold molar excess of benzyl bromide in the electrolysis reaction mixture of compounds Ia–d did not result in trapping of the anion; i.e., no formation of benzyldiphenylphosphine was observed even when the leaving group was phenoxy (Id). We conclude that the starting materials are significantly better substrates for nucleophilic attack than is benzyl bromide. It is interesting to note that we have observed a product that would have been expected had the intermediate anion been trapped. If the electrolysis reaction mixture containing benzyl bromide but which had been completely converted to the diphosphine product was allowed to stand overnight, white crystals were formed. Analysis of this product by ^{31}P NMR and the subsequent independent synthesis proved that the product was dibenzyldiphenylphosphonium bromide. We also found an equivalent amount of bromodiphenylphosphine in the supernatant liquid. A subsequent reaction using commercial tetraphenyldiphosphine demonstrated that the reaction shown in eq 10 was operative. A similar reaction has been previously reported in the literature.[11] We propose the mechanism detailed in equations 11 through 13 to account for the formation of these products.

$$Ph_2P\text{–}PPh_2 + 2PhCH_2Br \rightarrow (PhCH_2)_2P^+Ph_2Br + Ph_2PBr \qquad (10)$$

$$Ph_2P\text{–}PPh_2 + PhCH_2Br \rightarrow Ph_2P\text{–}P^+Ph_2(CH_2Ph)Br^- \qquad (11)$$

$$Br^-Ph_2P\text{–}P^+Ph_2(CH_2Ph) \rightarrow Ph_2PBr + Ph_2P\text{–}CH_2Ph \qquad (12)$$

$$Ph_2P\text{–}CH_2Ph + PhCH_2Br \rightarrow Ph_2P^+(CH_2Ph)_2Br^- \qquad (13)$$

Experimental Section

^{31}P NMR spectra were obtained on a Varian CFT 20 instrument and are reported by using the standard convention of shifts downfield of external 85% H_3PO_4 being positive.

Chlorodiphenylphosphine, Ia, was used as obtained from Aldrich Chemical Co. The purity was checked by ^{31}P NMR in which a single peak at +81.9 ppm ($CDCl_3$) was observed.

Bromodiphenylphosphine, Ib, was synthesized[12] from the reaction of 0.09 mol of chlorodiphenylphosphine with 0.19 mol of phosphorus tribromide, followed by a vacuum distillation which gave 18.3 g (72%) of product which boiled at 130–135 °C (0.15 torr): ^{31}P NMR +72.1 ppm ($CDCl_3$) (lit.[13] +70.8 ppm).

Fluorodiphenylphosphine, Ic, was synthesized[14] from the reaction of 0.09 moles of chlorodiphenylphosphine with 0.67 mol of sodium fluoride in acetonitrile, followed by a vacuum distillation. Fifteen grams (82.5%) of product was isolated at 127–133 °C (0.01 torr): ^{31}P NMR +169.1 ppm ($CDCl_3$) (lit.[14] +168.4 ppm).

Phenyl diphenylphosphinite, Id, was synthesized by the dropwise addition of a solution containing 0.11 mol of phenol and 0.11 mol of triethylamine in 200 mL of ether to a 500-mL solution of 0.11 mol of chlorodiphenylphosphine in ether. Following filtration and removal of the ether, 23.0 g (73%) of product was obtained by vacuum distillation at 183–189 °C (0.6 torr): ^{31}P NMR +110.8 ppm ($CDCl_3$); mass spectrum, *m/z* 278.0856 (M^+, calcd for $C_{18}H_{15}OP$ 278.0857).

Tetra-*n*-butylammonium bromide was purchased from Aldrich Chemical Co. and purified by recrystallization from benzene–hexane and dried under vacuum.[15]

Acetonitrile was purified by drying over phosphorus pentoxide for at least 24 h before distilling and storing over 3A molecular sieves.[16]

Cyclic voltammograms were obtained at room temperature on a Princeton Applied Research Model 173 potentiostat in combination with a Model 175 universal programmer and recorded on a PAR Model 9002A X-Y recorder. The cell[17] consisted of a Pt foil disk working electrode 7 mm in diameter surrounded by a Pt wire coil as the counter electrode. The reference electrode was a Ag wire in 0.1 M silver nitrate in acetonitrile and separated from the reaction chamber by a Vycor microporous frit and in communication with the working electrode through a Luggin capillary terminating within 2 mm of the working electrode. Dry acetonitrile solutions of 25 mL containing 0.1 M tetra-*n*-butylammonium perchlorate were added to the cell and flushed with dry nitrogen. Background CV scans were run to ensure that no electrochemical activity was present, and then the appropriate amount of compound (Ia–d) was added via a 100-L syringe.

The preparative electrolyses and coulometry experiments were carried out with an ECO Model 550 potentiostat equipped with a ECO Model 721 digital coulometer. The electrochemical cell consisted of an ECO Model 1000 electroprep cell equipped with a Monel cathode and a ruthenized titanium anode separated by a microporous glass separator. The reference electrode was a Ag wire in 0.1 M silver nitrate in acetonitrile separated from the catholyte by a microporous Vycor frit. In a typical experiment

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[9] Spanier, E. J.; Caroprreso, F. E. *J. Am. Chem. Soc.* **1970**, *92*, 3348.

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[16] Reference 15, p 68.

[17] Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142 (Figure 1).

the anolyte solution consisted of 200 mL of dry acetonitrile containing 0.1 M tetra-*n*-butylammonium bromide as electrolyte. The catholyte consisted of 200 mL of the above solution plus 0.882 g (0.004 mol) of chlorodiphenylphosphine. The anolyte and catholyte solutions were circulated from separate flasks by ECO Model 920 Teflon pumps and were continuously flushed with dry nitrogen. Yields were calculated by adding triphenylphosphine as an internal standard and subjecting the resulting solution to gas chromatographic analysis on a 5 ft × $^1/_8$ in. 3% SE30 on 80–100 mesh Chromosorb WHP column at 215. The detector response had been calibrated by an authentic sample of tetraphenyldiphosphine.[18] Tetraphenyldiphosphine was isolated by removing the solvent in vacuuo, dissolving the resulting oil in benzene and running this solution through a short silica gel column to remove the electrolyte salt, followed by recrystallization from benzene–hexane: mp 121 °C (lit.[19] 122 °C); ^{31}P NMR −14.4 ppm (Me_2SO-d_6). The isolated material was compared with authentic tetraphenyldiphosphine by observing identical gas chromatographic retention times and by spiking the isolated sample with authentic material and observing only a single peak. This spiking technique was also used in ^{31}P NMR analysis with the observation of only one resonance.

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Registry No. Ia, 1079-66-9; Ib, 1079-65-8; Ic, 20472-53-1; Id, 13360-92-4; phenol, 108-95-2.

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(18) Strem Chemical Co.

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Platinum-Catalyzed Asymmetric Hydroformylation with a Polymer-Attached Optically Active Phosphine Ligand

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A chiral ligand, analogous to 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dibenzophospholyl)butane (DBP-DIOP) (**5**), attached to linear and to cross-linked polymer supports was obtained either by copolymerization of (4*R*,5*R*)-2-(*p*-styryl)-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (**2**) with styrene (or with styrene and divinylbenzene) followed by phosphination with lithium dibenzophosphole or directly by copolymerization of (4*R*,5*R*)-2-(*p*-styryl)-4,5-bis[(dibenzophospholyl)methyl]-1,3-dioxalane (**4**) with styrene (or with styrene and divinylbenzene). Exchange of Pt(II) onto the polymers followed by the addition of stannous chloride gave polymer-supported catalysts which were used for asymmetric hydroformylation of a variety of olefins. Hydroforymlations utilizing the polymer-supported catalysts showed comparable rates and gave nearly the same optical yields as the homogeneous analogue **5**. However, lower branched to normal ratios were obtained from the polymer-supported catalysts, especially with those which were cross-linked. The soluble polymer-supported catalyst could be recovered by precipitation with diethyl ether and filtration. Reuse of this catalyst showed no loss in rate or selectivity. Recycling of the cross-linked polymer was achieved by simple filtration with slight loss in rate but no loss in selectivity.

The successful development of chiral transition-metal complexes for asymmetric synthesis has been followed by attempts to attach such complexes onto an insoluble polymeric support. The primary advantage of a polymer-supported catalyst is the ability to recover and reuse both the transition metal and the chiral optically active ligand.[1,2] However, very few chiral, polymer-bound ligands have been synthesized.[3-22] Most of these polymer-supported catalysts have been used for asymmetric hydrogenations; the few asymmetric hydroformylations reported generally gave low optical yields.[10,17] The asymmetric hydroformylation of styrene promoted by a catalyst obtained by supporting [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)]–$PtCl_2$–$SnCl_2$ onto a Merrifield resin gave the corresponding hydrotropaldehyde in 29% ee.[4a] However, attempts to carry out the reaction in the presence of a similarly supported [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dibenzophospholyl)butane (DBP–DIOP)]–$PtCl_2$–$SnCl_2$ catalyst failed to give reasonable conversions to aldehydes.[22] We were able to carry out an asymmetric hydroformylation reaction of styrene with an [*N*-(*tert*-butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM)]–$PtCl_2$–$SnCl_2$ catalyst bound to polystyrene beads.[3] Although branched to normal ratios were low (∼0.5), the corre-

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