Transformations of 1,3-di-*p*-tolyl-5-*p*-toluidinomethyl-1,3,5-diazaphosphorinane initiated by electrochemical oxidation at a glassy carbon electrode

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Electrochemical oxidation of 1,3-di-*p*-tolyl-5-*p*-toluidinomethyl-1,3,5-diazaphosphorinane at a glassy carbon anode yields 5,5'-spirobis(1,3-di-*p*-tolyl-1,3,5-diazaphosphoniarinane) perchlorate and 1,3-di-*p*-tolyl-5-*p*-toluidinomethyl-1,3-diaza-2-carbenia-5-phosphorinane perchlorate. The latter reacts on a Pt^{II} template to give a complex of a new diphosphine ligand.

Key words: α-aminomethylphosphines, electrochemical oxidation, carbocations, template reactions; ^1H, ^{13}C and ^{31}P NMR spectra.

Investigation of electrochemical properties of organic compounds incorporating several electroactive centers affecting one another is significant for both theoretical and synthetic electrochemistry. One can expect that electrochemical treatment of these substances, depending on the structure of their molecules, the effects of substituents at the electroactive centers, and the reaction conditions, would result in unusual transformations of the active species generated at an electrode (for example, initiation of intramolecular reactions and rearrangements) affording new types of products. α-Aminomethylphosphines containing a PCH_2N structural fragment provide an example of compounds with several functional groups in their molecules.[1,2]

Previously it has been found[3] that electrochemical oxidation of 1,3-di-*p*-tolyl-5-*p*-toluidinomethyl-1,3,5-diazaphosphorinane (**1**) at a mercury electrode results in its transformation into a new diphosphine ligand and in the formation of the corresponding complex of mercury(II), whose yield is higher than that obtained in the chemical synthesis (reaction of **1** with mercury(II) perchlorate). It is not inconceivable that the yield of the product increases due to parallel electrochemical synthesis of the ligand. To verify this suggestion and also to study the properties of polyfunctional radical cations and the possibility of electrochemical synthesis of new phosphine ligands, we have studied the anodic oxidation of compound **1** at an inert insoluble glassy carbon electrode.

Results and Discussion

Voltammetric studies showed that during the anodic reduction of compound **1**, only one oxidation wave is present in the working region of potentials (up to 2.0 V). The fact that the height of the limiting current of this wave depends linearly on the square root of the rate of the potential sweep indicates that its limiting current is a diffusion current. The half-wave potential $E_{1/2}$ found from the dependence of E on $\log i/id - i$ is 710 mV. The absence of the reverse wave over the whole range of rates of potential sweep chosen (0.05—10 V s^{-1}) indicates that the anodic oxidation of **1** is generally irreversible.

The facts that only one oxidation wave appears and the anodic process is irreversible as well as the low number of electrons transferred to the electrode (n = 0.6) attest that the anodic oxidation of **1** at an inert electrode occurs by an *EC*-mechanism and is followed by fast chemical reactions that might involve all the electroactive centers in the molecule.

More detailed information on the regularities of the anodic oxidation of **1** was gained from the results of its preparative oxidation. This process was carried out at a glassy carbon electrode in acetonitrile with the anodic potential varied from 0.8 to 1.6 V. The exhaustive oxidation required 0.72 F of electricity per mole of the organophosphorus compound.

The electrolysis of compound **1** affords organophosphorus compounds of various types. Instead of the ex-

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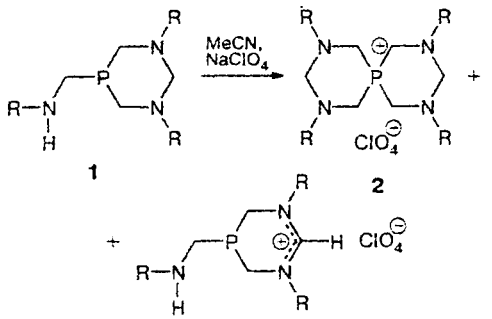
pected usual products of electrooxidation of phosphines, diphosphine with an aminomethyl bridge,[3] biphosphonium salts,[4] or aminophosphonium salts,[5] we isolated compounds **2** and **3**.

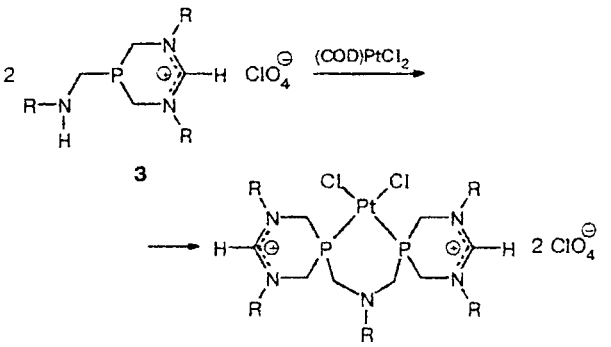


The structures of products **2** and **3** were determined by IR and ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectrum of compound **2**, the methylene protons of the P—CH_2—N fragment are manifested as an A_2X-system, and the methylene protons of the N—CH_2—N fragment are exhibited as a singlet; this indicates that the spirobicyclic cation of **2** has a symmetrical structure in solution.

Compound **3** is a white finely crystalline powder. The IR spectrum of this compound contains absorption bands corresponding to its main functional groups including a band at 1665 cm^{-1} due to the N=CH^+—N conjugated fragment.[6] The formation of the carbocation is also indicated by the fact that the ^{1}H and ^{13}C NMR spectra of compound **3** contain no signals for the methylene bridge between the N atoms but, instead, they contain signals markedly shifted downfield and corresponding to a methine bridge. In addition, on going from compound **1** to compound **3**, the mutual arrangement of the ^{13}C NMR signals for the C atoms of the tolyl substituents at the ring N atoms changes. Thus the signal due to the *p*-C atom is appreciably shifted downfield ($\Delta\delta$ 14.9), whereas the signal for *ipso*-C is displaced upfield ($\Delta\delta$ −7.8). Similar changes have been observed upon protonation of *p*-toluidine.[7] The signals corresponding to the C atoms of the tolyl substituent at the exocyclic N atom do not change significantly on going from compound **1** to **3**, nor does the ν(NH) value in the IR spectra. The data of ^{31}P NMR spectroscopy imply that the coordination of the P atom is retained and the unusually high-field position of the signal of compound **3** compared to that of **1** ($\Delta\delta$ −42.2) is associated, apparently, with the appearance of a planar carbocationic fragment in the ring. Signals in the region of −80 to −100 ppm are observed in the spectra of some cyclic aminomethylphosphines.[8]

The nucleophilic properties of the P and N atoms in the exocyclic substituent in compound **3** are retained, despite the presence of a strong electrophilic center. In fact, when phosphine **3** reacts with (cyclooctadiene)dichloroplatinum, cyclooctadiene is readily displaced, and the formation of the P,P′-complex is accompanied by intramolecular nucleophilic substitution and affords a complex incorporating a new diphosphine ligand, *cis*-*p*-tolylbis(1,3-di-*p*-tolyl-1,3-diaza-5-phosphorinan-2-ylium-5-ylmethyl)amine-dichloroplatinum(II) (**4**).



Previously[3] similar template transformations have been observed in connection with the formation of complexes of the initial compound **1**. The change of the chemical shift of compound **4** with respect to that of **3** ($\Delta\delta$ 42.5) and the magnitude of the Pt—P spin-spin coupling constant indicate that the electron density is displaced from the P atom, as is also typical of noncharged ligands of this type.[9] Thus, it can be seen that the positive charge of phosphine **3** is localized only on the N=CH^+—N fragment, whereas the rest of the heteroatoms (the P atom and the exocyclic N atom) do not interact with the carbocationic center.

These results suggest that the first step of the electrochemical oxidation of compound **1** involves removal of the lone electron pair from the ring N atom, which affords an unstable radical cation. This radical cation is stabilized, apparently, by two independent pathways. One of them involves elimination of a proton from the NCH_2N fragment and further oxidation of the resulting radical to the carbocation **3**. A similar mechanism has been proposed for the electrooxidation of cyclic 1,3-diamines.[10] Compound **2** results from the second stabilization pathway, which involves cleavage of the labile bonds in the P—CH_2—N fragment and subsequent interaction of the intermediates thus formed with an initial molecule of **1** with the transfer of positive charge to the most nucleophilic atom in the molecule.

Thus, the electrochemical behavior of aminomethylphosphines differs appreciably from that of the phosphines studied previously[4,5] and opens the way to the synthesis of new unusual organophosphorus compounds.

Experimental

Voltammetric measurements were carried out in a 10-mL glass cell in CH_2Cl_2 using Et_4NClO_4 as the supporting electrolyte. A PI-50-1 potentiostat served as the source of the polarizing voltage; the voltammetric curves were recorded using an S9-8 digital data storage oscillograph. The rate of the potential sweep was 0.05—10 V s^{-1}. A platinum disc (with a working surface area of 0.2 cm^2) served as the anode, and bottom mercury served as the auxiliary electrode. An $Ag/AgNO_3$ (0.01 *M* in MeCN) silver electrode was used as the reference electrode. Oxygen was removed from solutions to be studied by passing dry argon through them. The number of electrons transferred from a molecule of the depolarizer to the electrode was determined by comparing the limiting currents for compound **1** and a model compound, trimesitylphosphine, which produces a fully reversible single-electron wave.[11]

^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer (161.162 MHz), and ^1H NMR spectra were obtained using a Bruker WM-250 instrument (250.400 MHz). IR spectra were measured on a Specord-M-80 spectrophotometer.

The preparative electrooxidation of **1** was performed in a 100-mL glass cell with a porous diaphragm separating the cathode and anode areas. A glass-carbon cylinder (of the SU-2000 tradename) with a working surface area of 50 cm^2 served as the anode; a nickel helix with a surface area of 20 cm^2 was used as the cathode. A saturated solution of $NaClO_4$ in MeCN served as the catholyte. The working solution (anolyte) was prepared by dissolving 4.03 g (0.01 mol) of **1** and 0.6 g (0.005 mol) of $NaClO_4$ in 80 mL of MeCN. The electrolysis was carried out under amperostatic conditions at a current density of 0.2—0.4 mA cm^{-2}; the anodic potential varied from 0.8 to 1.6 V.The amount of electricity passed through the electrolyte was 0.19 A h. After the electrolysis, the solvent was evaporated, the residue was dissolved in 50 mL of CH_2Cl_2, and 20 mL of hexane was added to it. The resulting precipitate (compound **2**) was filtered off and washed with methanol. The filtrates were combined, and the solvent was removed *in vacuo*. To the solid residue, 15 mL of a 2 : 1 EtOH—CH_2Cl_2 mixture was added. The resulting finely crystalline precipitate of compound **3** was filtered off and washed with ether.

5,5′-Spirobis(1,3-di-*p*-tolyl-1,3,5-diazaphosphoniarinane) perchlorate (2). Yield 1.2 g (19.2%, based on the substance), m.p. 139—143 °C (from a mixture of ethanol and ethyl acetate). Found (%): C, 64.07; H, 6.17; Cl, 5.52; N, 9.18; P, 5.35. $C_{34}H_{40}ClN_4O_4P$. Calculated (%): C, 64.30; H, 6.30; Cl, 5.60; N, 8.83; P, 4.89. ^{31}P NMR (DMF), δ: −16.57. ^1H NMR (CD_3CN), δ: 2.26 (s, 12 H, CH_3); 4.39 (d, 8 H, PCH_2N, $^2J_{PH}$ = 4.3 Hz); 4.80 (s, 4 H, NCH_2N); 6.84 (d, 8 H, *o*-HC(Ar), $^2J_{HH}$ = 8.5 Hz); 7.09 (d, 8 H, *m*-HC(Ar), $^2J_{HH}$ = 8.5 Hz). IR, ν/cm^{-1}: 1100 (ClO_4), 1610 (Ar).

1,3-Di-*p*-tolyl-5-toluidinomethyl-1,3,5-diazaphosphorinan-2-ylium perchlorate (3). Yield 0.46 g (12.3%, based on the substance), m.p. 210—216 °C (from ethanol). Found (%): C, 58.66; H, 5.64; Cl, 7.72; N, 8.45; P, 6.72. $C_{25}H_{29}ClN_3O_4P$. Calculated (%): C, 59.82; H, 5.78; Cl, 7.08; N, 8.38; P, 6.18. ^{31}P NMR (DMF, MeCN), δ: −90.65. ^1H NMR (CD_3CN), δ: 2.19 (s, 3 H, CH_3*); 2.39 (s, 6 H, CH_3); 3.60 (d, 2 H, PCH_2N*, $^2J_{PH}$ = 6.6 Hz); 4.08 (dd, 2 H, PCH_AN, $^2J_{PH}$ = 4.6 Hz, $^2J_{AB}$ = 15.1 Hz); 4.23 (dd, 2 H, PCH_BN, $^2J_{PH}$ = 10.0 Hz, $^2J_{AB}$ = 15.1 Hz); 6.64 (d, 2 H, Ar—H*-*o*, $^2J_{HH}$ = 8.4 Hz); 6.96 (d, 2 H, Ar—H*-*m*, $^2J_{HH}$ = 8.4 Hz); 7.36 (d, 4 H, Ar—H, $^2J_{HH}$ = 8.8 Hz); 7.37 (d, 4 H, Ar—H, $^2J_{HH}$ = 8.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 24.21 (qt, 1 C, CH_3*, $^1J_{CH}$ = 124.9 Hz, $^3J_{CH}$ = 4.4 Hz); 24.70 (qt, 2 C, CH_3, $^1J_{CH}$ = 125.7 Hz, $^3J_{CH}$ = 4.0 Hz); 40.37 (td, 1 C, PCH^*_2N, $^1J_{CH}$ = 141.0 Hz, $^1J_{CP}$ = 10.5 Hz); 45.85 (td, 2 C, PCH_2N, $^1J_{CH}$ = 146.8 Hz, $^1J_{CP}$ = 29.1 Hz); 117.21 (d, 2 C, C*(Ar)-*o*, $^1J_{CH}$ = 155.6 Hz); 127.70 (d, 4 C, C(Ar)-*o*, $^1J_{CH}$ = 163.9 Hz); 129.62 (br.s, 1 C, C*(Ar)—Me); 133.82 (d, 2 C, C*(Ar)-*m*, $^1J_{CH}$ = 155.6 Hz); 134.39 (d, 4 C, C(Ar)-*m*, $^1J_{CH}$ = 161.3 Hz); 142.82 (br.s, 2 C, C(Ar)—N); 145.81 (br.s, 2 C, C*(Ar)—Me); 149.9 (br.s, 2 C, C*(Ar)—N); 156.50 (d, 1 C, N=CH—N, $^1J_{CH}$ = 199.1 Hz). IR, ν/cm^{-1}: 1100 (ClO_4); 1610 (Ar); 1665 (N=C); 3400 (N—H).

***cis-p*-Tolylbis(1,3-di-*p*-tolyl-1,3,5-diazaphosphorinan-2-ylium-5-ylmethyl)aminedichloroplatinum(II) (4).** A solution of compound **3** (0.193 g, 0.4 mmol) in 5 mL of acetonitrile was added to a solution of $CodPtCl_2$ (0.072 g, 0.2 mmol) in 5 mL of acetonitrile. The solvent was removed *in vacuo*, and a mixture of acetone and diethyl ether (1 : 1) was added. The orange-colored powder of **4** (0.19 g, 78%) was filtered off and washed with diethyl ether, m.p. 220—225 °C. Found (%): C, 44.49; H, 4.45; Cl, 12.48; N, 6.46; P, 5.15. $C_{43}H_{49}Cl_4N_5O_8P_2Pt$. Calculated (%): C, 44.41; H, 4.22; Cl, 12.22; N, 6.02; P, 5.34. ^{31}P NMR (DMF, MeCN), δ: −48.19 ($^1J_{PtP}$ = 3468.3 Hz). ^1H NMR (CD_3CN), δ: 2.42 (s, 3 H, CH_3**); 2.46 (s, 12 H, CH_3); 4.96 (br.s, 4 H, PCH_2N**); 5.09 (dd, 4 H, PCH_AN, $^2J_{PH}$ = 7.0 Hz, $^2J_{AB}$ = 15.3 Hz); 5.26 (dd, 4 H, PCH_BN, $^2J_{PH}$ = 5.3 Hz, $^2J_{AB}$ = 15.3); 6.69 (d, 2 H, Ar—H**-*o*, $^2J_{HH}$ = 8.2 Hz); 6.87 (d, 2 H, Ar—H**-*m*, $^2J_{HH}$ = 8.2 Hz); 7.32 (d, 8 H, Ar—H, $^2J_{HH}$ = 8.3 Hz); 7.63 (d, 8 H, Ar—H, $^2J_{HH}$ = 8.3 Hz). IR, ν/cm^{-1}: 1100 (ClO_4); 1610 (Ar); 1670 (N=C).

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* The atoms belonging to the exocyclic aminomethyl substituent.

** The atoms belonging to the bridging aminomethyl fragment.

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