where the Fe^{II}TPP is formed so that no catalytic reduction ensues until the potential approaches 0.1 V where the Fe^{II}TPP–O$_2$ adduct *is* reducible. (The final wave in Figure 12C arises from the reduction of the second form of adsorbed FeTPP that does not participate in the catalysis.)

The behavior shown in Figures 9F, 10, and 12 demonstrates the lack of reduction of O$_2$ by the Fe^{II}TPP which is generated at potentials positive of 0.1V. This behavior provides strong evidence against an alternative reaction mechanism in which the first step following the electroreduction of the catalyst is simple, outer-sphere electron transfer between Fe^{II}TPP and O$_2$. Such a mechanism has been proposed for the catalysis of O$_2$ reduction by iron porphyrins in solution,[9] but it can be ruled out for adsorbed FeTPP on the basis of the reaction pattern shown in Figures 9F, 10, and 12. The behavior of the adsorbed FeTPP and FeTMPyP catalysts, in which reduction of the adsorbed catalyst occurs at potentials ahead of those where the catalyzed reduction of O$_2$ proceeds, is the same as that exhibited by the corresponding cobalt porphyrin, CoTPP, where the reduction of Co^{III}TPP to Co^{II}TPP occurs at potentials much more positive than those where CoTPP serves as a catalyst for the reduction of O$_2$.[33] Thus, the behavior of iron and cobalt porphyrins in catalyzing the electroreduction of O$_2$ can be rationalized by means of a single reactivity pattern: The catalytic reduction of O$_2$ can occur at potentials no more positive than that at which the metal center in the metalloporphyrin is reduced from the +3 oxidation state, which does not interact with O$_2$, to the +2 oxidation state, which does. For cobalt porphyrins, this potential is much more positive than that where the electroreduction of O$_2$ is observed. The latter potential corresponds to the intrinsic reduction potential of the cobalt porphyrin–dioxygen adduct, which is evidently significantly more negative than the formal potential of the Co^{III}/Co^{II} couple of the cobalt porphyrin. In the case of iron porphyrins, E_2 (reaction 4) is more positive than E_1 (reaction 2) (except at low pH values). The result is a close correspondence between the potential where the iron(III) center in the catalytically relevant adsorbed porphyrin is reduced in the absence of O$_2$ and that where the catalyzed reduction of O$_2$ appears. The apparent mismatch between these two potentials that was emphasized in previous studies[10] of several iron porphyrins has been shown in the present work to disappear when adequate account is taken of the effect of adsorption on graphite on the formal potentials of the iron porphyrins.

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Chemical and Electrochemical Reduction of Binuclear Platinum Phosphine Complexes

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Two synthetic methods are described to produce platinum(0) complexes that contain two metal atoms held together by bridging phosphine ligands. Both platinum(I) and platinum(II) complexes are reduced by using chemical and electrochemical techniques to produce the desired platinum dimers. The electrochemistry and the solution chemistry of these complexes are investigated by cyclic voltammetry and NMR experiments. The formation of platinum hydride complexes is shown to be an important step in the electrochemical reactions.

Introduction

Platinum has played a major role in the catalytic rearrangement of hydrocarbons.[1] For that reason the study of platinum complexes has been and continues to be important. In particular, the platinum complexes that contain hydrocarbon units have been investigated as possible homogeneous complexes that may mimic intermediates proposed to be present on a platinum surface during catalysis.[2] Recently, both platinum(0) phosphine complexes[3] and platinum phosphine dimers[4] have received much attention because of their interesting reaction chemistry and their own potential as catalysts.

We became particularly intrigued with the report of a Pt(0) dimer, Pt$_2$(dppm)$_3$, where dppm = bis(diphenylphosphino)methane,[5,6] which readily participated in oxidative addition reactions with iodoalkanes, yet was stable enough to be characterized by crystallographic methods.[7] Keeping two platinum(0) atoms adjacent to one another with bridging phosphine ligands makes this dimer more analogous to metallic sites on a platinum surface than previously reported platinum dimers. So far, only one other platinum(0) dimer has been isolated.[8] Therefore, we sought to

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develop a general method of synthesis for platinum(0) dimers by first investigating reactions that would produce the well-characterized $Pt_2(dppm)_3$. The three reported synthetic routes for this dimer include (1) the reduction of $Pt(dppm)Cl_2$ or $Pt(cod)Cl_2$ (where cod = 1,5-cyclooctadiene) by sodium tetrahydroborate in the presence of excess dppm in aqueous ethanol, (2) the treatment of $Pt(PPh_3)_4$ in ethanol by excess dppm, and (3) the reduction of $Pt_2(\mu\text{-dppm})_2Cl_2$ by ethanolic KOH in the presence of excess dppm.[5] Thus, we began by investigating the chemical and electrochemical reduction of $Pt_2Cl_2(dppm)_2$ (**1**) and $PtCl_2(dppm)$ (**2**). We now report the results of our initial investigations.[9]

Experimental Section

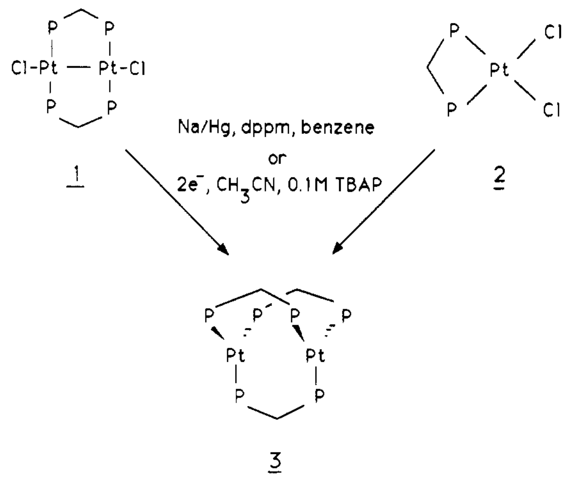
Preparation of Compounds. $Pt_2Cl_2(dppm)_2$ (**1**), $PtCl_2(dppm)$ (**2**), $Pt(dppm)_2$ (**4**), $[Pt_2(\mu\text{-dppm})_2Cl(\eta^1\text{-dppm})]Cl$ (**5**) $[Pt(dppm)_2]Cl_2$ (**7**), $[Pt_2H(\mu\text{-dppm})_2(\eta^1\text{-dppm})]Cl$ (**8**), and $Pt_2H_3(dppm)_2$ (**9**) were prepared by literature methods.[4a,10,11] Bis(diphenylphosphino)methane (Strem), hydrogen hexachloroplatinic acid (Aldrich), and cyclooctadiene (Aldrich) were used as received. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide (Aldrich) and perchloric acid. It was recrystallized five times from ethyl acetate/hexane and dried in vacuo. Reagent grade benzene (EM Science) was refluxed over potassium prior to distillation under a nitrogen atmosphere. Hexane (EM Science) was refluxed over sodium prior to use. HPLC grade acetonitrile (EM Science) was refluxed and distilled from potassium permanganate and lithium carbonate, potassium bisulfate, calcium hydride, and finally phosphorus pentoxide.

$Pt_2(dppm)_3$ (3) from the Sodium Reduction of 1. All manipulations were done under an inert atmosphere by using vacuum line and Schlenk ware techniques and a recirculating drybox (Vacuum Atmospheres). In a typical reaction, sodium metal (0.01 g, 0.43 mmol) is dissolved in mercury (0.4 mL) in a 100-mL three-necked flask. After 20 mL of freshly distilled benzene is added, the mixture is cooled in an ice–water bath for 20 min. **1** (0.2 g, 0.16 mmol) and dppm (68 mg, 0.18 mmol) are added to the partially frozen mixture as solids. The ice bath is removed, and the mixture is allowed to warm to room temperature while being stirred. The yellow mixture slowly turns to a deep red solution over a period of 2 h. The grayish white solid that is present is allowed to settle, and the red benzene solution is transferred to another three-necked flask by syringe. Removal of the solvent under vacuum and subsequent washing of the residue with freshly distilled hexane yielded 0.175 g (70% yield based on **1**) of a dark red solid. This solid was identified as **3** by ^1H and ^{31}P NMR and UV-vis spectroscopy.[5]

$Pt_2(dppm)_3$ (3) from the Sodium Reduction of 2. By use of the same procedure as described in the previous paragraph, **2** (0.2 g, 0.31 mol) and dppm (60 mg, 0.16 mmol) were added as solids to the partially frozen sodium amalgam–benzene mixture. The red solid was isolated (0.135 g, 57% yield based on **2**) and identified as before to be **3**.

$[Pt_2(\mu\text{-dppm})_2(\eta^1\text{-dppm})_2][PF_6]_2$ (6a). To a suspension of **1** (30 mg, 0.24 mmol) in 4 mL of methanol was added a suspension of dppm (38 mg, 0.98 mmol) in 10 mL of methanol. The mixture was stirred at room temperature for 15 min, during which time the solid dissolved to form a clear yellow solution. The solution was stirred for another hour at room temperature, after which a solution of NH_4PF_6 (0.14 g, 1.3 mmol) in methanol was added. A yellow precipitate formed, and solvent was removed under reduced pressure. The yellow powder was washed with water and ether and then dissolved in 3 mL of acetone. Careful addition of hexane produced yellow crystals (103 mg, 19% yield). The product was identified by comparison of its ^1H and ^{31}P NMR spectra with the spectra reported for known complexes of the type $[Pt_2(\mu\text{-dppm})_2L_2]^{2+}$ where L = Me_2PhP, Ph_2MeP, and PPh_3.[14] ^1H NMR (acetone-d_6): δ 5.62 (multiplet, $^3J(Pt–H) = 55$ Hz, PCH_2P) 6.56–8.17 (complex multiplet, $P–C_6H_5$). ^{31}P NMR (acetone-d_6): δ –98.54 (septet, $^1J(P–F) =$ 710 Hz, PF_6), 21.7 (d, $J(P–P) = 17$ Hz, η^1-dppm), 40.0 (t $^1J(Pt–P_{A,B})$ = 2818 Hz, μ-dppm), 54.6 ($^1J(Pt_A–P) = 939$ Hz, $^1J(Pt_B–P) = 1713$ Hz, η^1-dppm). Elemental analysis was not attempted because, in solution, this compound is in equilibrium with its monocation, which forms by dissociation of one dppm ligand. Even when crystals were obtained, the proton and phosphorus NMR spectra indicated the presence of the monocation.

Scheme I



$[Pt_2(\mu\text{-dppm})_2(\eta^1\text{-dppm})_2][ClO_4]_2$ (6). The method of preparation was the same as described for **6a** except for the addition of lithium perchlorate in place of ammonium hexafluorophosphate. *Caution! Perchlorate salts are a known explosive hazard. Ones containing organic ligands are particularly dangerous. Only small amounts should be prepared, and use of metal spatulas should be avoided.*[12] The quantities of reagents used were 82 mg (0.07 mmol) of **1**, 65 mg (0.17 mmol) of dppm, and 0.14 g (1.3 mmol) of lithium perchlorate. After recrystallization, the product obtained (124 mg, 87% yield) was identified by its ^{31}P NMR spectrum, which matched the one observed for **6a** with the exception of the absence of the signal due to the hexafluorophosphate anion. Elemental analysis was not attempted on this compound for the same reason given above for **6a**.

NMR Spectroscopy. Proton NMR spectra were recorded on a General Electric QE-300 NMR spectrometer at room temperature using a 5-mm probe. Samples were dissolved in $CDCl_3$, CD_2Cl_2, CD_3OD, or acetone-d_6 as indicated. All deuterated solvents were purchased from Aldrich Chemical Co. and used without further purification. TMS (Aldrich) served as an internal reference.

Phosphorus NMR spectra were recorded at room temperature on a General Electric GN-300 NMR spectrometer using a 10-mm probe. Samples were dissolved in $CDCl_3$, CD_2Cl_2, C_6D_6, CD_3CN, CD_3OD, or acetone-d_6 (Aldrich) as indicated. All data were obtained by using broad-band proton decoupling and a recycle delay of 5 s. A solution of TMP in deuteriobenzene was used as an external reference.

Electrochemical Measurements. Cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) experiments were performed with a Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat. All CV experiments were performed in a 0.1 M TBAP solution of acetonitrile by using a three-electrode system consisting of a hanging-mercury-drop (HMDE) working electrode, a platinum-wire counter electrode, and a silver/silver nitrate reference electrode that was isolated from the working solution by a Vycor plug. The silver/silver nitrate reference electrode consisted of a silver wire (BioAnalytical Systems) in an acetonitrile solution that was 0.01 M in silver nitrate and 0.10 M in TBAP. The $E_{1/2}$ value for this reference electrode vs ferrocene was +0.10 V. Measurements were made at 25 °C under deoxygenated conditions (Ar). The electrode potentials were calibrated by measuring the ferrocene/ferrocenium couple at the end of the experiment. CPE experiments were carried out under the same conditions using a mercury-pool working electrode. Solutions were stirred by a stream of argon saturated with acetonitrile. Preelectrolysis of the electrolyte solution was done prior to the addition of **1** or **2** to the solution.

Electrochemical Synthesis of 3 Using 1. The cell solution was prepared by dissolving dppm (7.45 mg, 0.02 mmol) in 10 mL of a 0.1 M solution of TBAP in acetonitrile. After preelectrolysis of this solution at a potential of –2.15 V for 1 h, **1** (22.2 mg, 0.02 mmol) was added. As **1** dissolved, the solution turned from colorless to bright yellow. At an applied potential of –2.15 V, the solution slowly turned to pale yellow while a red precipitate formed on the surface of the mercury-pool electrode. After the cell was turned off and the flow of argon was adjusted to pass over the surface of the solution, the solvent containing the TBAP and any unreacted **1** and dppm was removed by syringe. The red solid was washed once with dry, deoxygenated acetonitrile and then dissolved in 5 mL of dry, deoxygenated benzene. The resulting dark red solution

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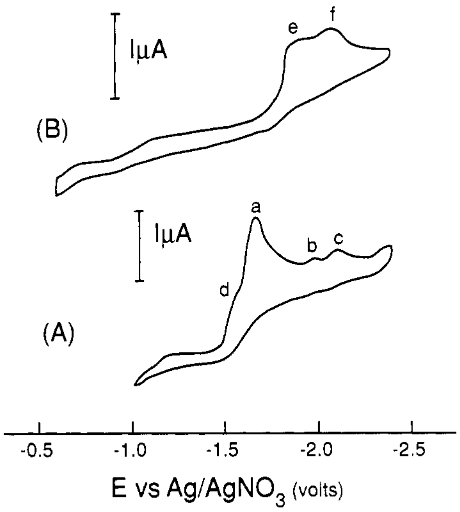

Figure 1. Cyclic voltammograms of **1** with dppm (A) and of **1** without dppm (B) at an HMDE in 0.1 M TBAP/CH_3CN (scan rate 0.1 V/s).

was transferred to a clean, dry three-necked flask filled with argon. After the flask was closed, it was moved into the drybox where the benzene was removed under vacuum. The red reaction residue was washed with dry, deoxygenated hexane and dried under vacuum for 1 h, yielding 11 mg (40% based on **1**) of a red solid. This solid was identified by ^1H and ^{31}P NMR spectroscopy to be a pure sample of **3**.

Electrosynthesis of 3 using 2. By use of the same reaction conditions as described in the previous paragraph, **2** (18.5 mg, 0.03 mmol) was added to the preelectrolyzed cell solution (−2.25 V for 1 h) containing dppm (11.5 mg, 0.03 mmol). After 5 h of electrolysis at a potential of −2.25 V, the red precipitate was isolated (9 mg, 41% yield based on **2**) and identified as **3** by NMR spectroscopy.

Results

The routes chosen for the chemical and electrochemical syntheses of $Pt_2(dppm)_3$ (**3**) are shown in Scheme I. For the electrochemical reduction of **1** and **2**, a large negative potential (−2.0 V) was anticipated because of the reported reduction potential of the related Pt(II) complex, $PtCl_2(PPh_3)_2$.[13] Sodium amalgam was chosen as the reducing agent to simulate this applied negative potential with a chemical system.

Sodium Amalgam Reduction of $Pt_2Cl_2(dppm)_2$ (1) and $PtCl_2$(dppm) (2). Sodium amalgam reductions are well-known to be reliable, quick, and useful in either polar or nonpolar solvents. Using benzene as the solvent provided two major advantages: (1) Pt(0) complexes are readily soluble in benzene whereas the Pt(I) and Pt(II) precursors are not, and (2) the NaCl formed during the reaction precipitates from the solution. By the end of the reaction, only the desired Pt(0) complexes would remain in solution and thereby be easily separated from the reaction residue.

The sodium amalgam reduction of a solution of **1** and dppm in benzene readily yielded the desired platinum(0) dimer, **3**. This dimer was also obtained when a solution containing **2** and dppm was treated with sodium amalgam. In addition, a minor amount of $Pt(dppm)_2$ (**4**) was formed, which was identified by a separate synthesis of **4** and its ^{31}P NMR spectrum. No minor products were found in the isolated product from the reaction using **1**, which produced **3** in high yield.

Cyclic Voltammetry of 1. The cyclic voltammogram of complex **1** in a solution of acetonitrile containing 1 molar equiv of dppm is shown in Figure 1A. The largest peak current occurs at a potential of −1.64 V (see peak a). Two smaller peaks are observed at −1.93 V (b) and −2.08 V (c). In addition, there is a shoulder peak at −1.52 V (d). Figure 1B is the cyclic voltammogram of the solution of complex **1** in acetonitrile without added dppm. The cathodic peaks are less well defined but have current maxima at −1.84 V (e) and −2.07 V (f). A comparison of Figure 1A with Figure 1B shows that the only maxima in common are peaks c and f, which occur at −2.08 V and −2.07 V, respectively. It is clear that the species producing the largest reduction peak in Figure 1A is not complex **1**. This difference led to further investigation of the cell solution by ^{31}P NMR spectroscopy.

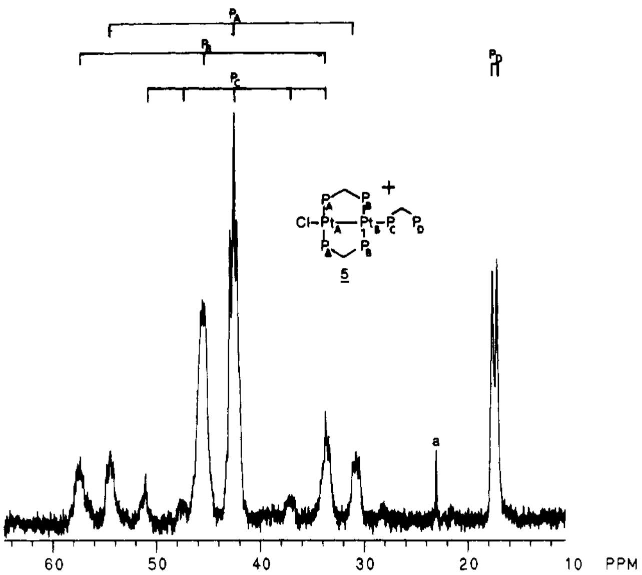

Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **5** in $CDCl_3$ recorded at 21 °C. Peak a is due to uncoordinated dppm. Chemical shifts and coupling constants are reported in Table I.

Table I. $^{31}P\{^1H\}$ NMR Chemical Shifts and Coupling Constants for $[Pt_2Cl(\mu\text{-dppm})_2(\eta^1\text{-dppm})]^+$ in $CDCl_3$[a]

μ-dppm

$\delta(P^A)$, ppm	$^1J(Pt_A-P^A)$, Hz	$\delta(P^B)$, ppm	$^1J(Pt_B-P^B)$, Hz	N, Hz
42.6	2879	45.7	2885	74

η^1-dppm

$\delta(P^C)$, ppm	$^1J(Pt_A-P^C)$, Hz	$^1J(Pt_B-P^C)$, Hz	$\delta(P^D)$, ppm	$J(P^C-P^D)$, Hz
42.6	1271	2155	17.4	52

N', Hz

calc	found
3248	3261

[a] Chemical shifts are relative to external TMP.

The ^{31}P NMR spectrum shown in Figure 2 was obtained on a solution of **1** and dppm (each 0.03 mM) in deuteriochloroform. Except for a better signal to noise ratio, the spectrum shown in Figure 2 is identical with the one obtained from the acetonitrile solution used in electrolysis, i.e. 0.002 mM each in **1** and dppm.

The four phosphorus atoms in **1** are magnetically equivalent, producing a single ^{31}P resonance with complex Pt satellite peaks.[4a] From Figure 2 it can be seen that the major platinum complex in solution is not **1**. Integration of the spectrum yielded a 1:5 ratio between the upfield doublet and the lower field multiplets including satellite peaks. No platinum satellites are observed with the upfield doublet, and thus it is assigned to an uncoordinated phosphorus atom. The lower field multiplets belong to phosphorus atoms that are coordinated to platinum atoms. The sharp singlet at 23 ppm is due to free dppm. Comparison with the spectra for the complexes $[Pt_2Cl(dppm)_2PPh_3]Cl$[10] and $[Pt_2H(dppm)_3][PF_6]$[11] leads to assignment of the dimer $[Pt_2Cl(\mu\text{-dppm})_2(\eta^1\text{-dppm})]Cl$ (**5**) for the spectrum in Figure 2. Chemical shifts and coupling constants shown in Figure 2 follow those in ref 11. The coupling constants are given in Table I and compare well with reported values.[11]

The formation of **5** occurs rapidly upon mixing **1** with dppm in solution and is a result of one chloride ligand being substituted by one dppm molecule, as reported for other Pt(I) dimers as well.[14,15] Uncoordinated dppm remains in the solution even though a 1:1 molar ratio of **1** to dppm was used to prepare the NMR sample. Some **1** must also be present in a small amount but is difficult to observe at low concentration, since the central and

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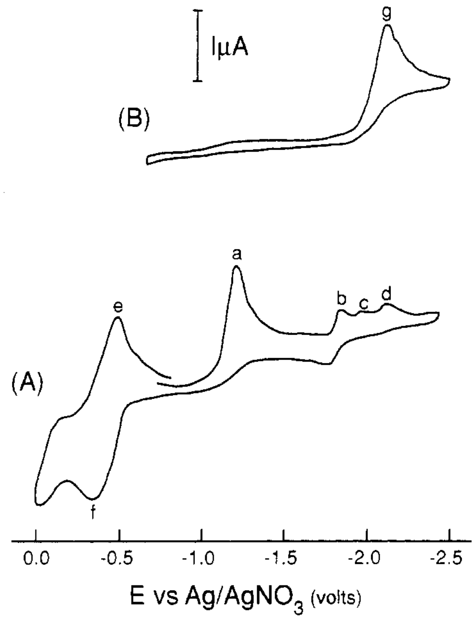

Figure 3. Cyclic voltammograms of **2** with dppm (A) and of **2** without dppm (B) at an HMDE in 0.1 M TBAP/CH_3CN (scan rate 0.1 V/s).

strongest resonance of **1** falls under the resonance of the low-field multiplet of **5** in the spectrum shown in Figure 2.

A small cathodic peak at −1.84 V (peak e, Figure 1) indicates the presence of a small amount of **1** in addition to **5**. Also present in the cyclic voltammogram in Figure 1A is a shoulder at −1.52 V (peak d), which is assigned to the dication $[Pt_2(\mu\text{-dppm})_2(\eta^1\text{-dppm})_2]^{2+}$ (**6**). A separate synthesis of this dication and a subsequent CV experiment confirmed this assignment. Since existence of this dication in polar solvents is known,[16] it is not suprising that some should be formed under the polar conditions of the cell solution.

The oxidation of free chloride ion was observed only in solutions containing **1** and dppm when the positive sweep direction of the cyclic voltammogram was increased to 0.0 V. The quasi-reversible oxidation/reduction peaks due to the chloride ion/Cl_2 couple were present at −0.31 and −0.58 V.

Cyclic Voltammetry of 2. When equimolar quantities of complex **2** and dppm are added to the cell solution, the cyclic voltammogram shown in Figure 3A is produced. Current maxima are observed at −1.16 V (a), −1.80 V (b), −1.93 V (c), and −2.07 V (d) in addition to the quasi-reversible oxidation/reduction peaks at −0.32 V (e) and −0.44 V (f). The quasi-reversible peaks correspond to the free chloride ion/Cl_2 couple and indicate the occurrence of a ligand substitution reaction. CV of a solution of tetrabutylammonium chloride (TBAC) in acetonitrile further clarified these peaks. A broad oxidation peak at −0.40 V was seen with two reduction peaks at −0.55 and −0.33 V when the concentration of TBAC was greater than 1.5 mM. It was apparent from the size of the oxidative peak (peak f, Figure 3A) that another species was also being oxidized at the same potential as the chloride ion, similar to that observed in the cyclic voltammogram of $(PPh_3)_2PtCl_2$.[17] We believe that in the present case the oxidation is related to the combined presence of chloride ion and the dppm ligand and is not due to the reduced platinum species **3**. Voltammetry on a solution containing **3** as the only platinum complex showed a single oxidation peak at −0.76 V, which did not overlap with the peak assigned to the oxidation of the chloride ion. In addition, when only dppm and TBAP were present in the cell solution, a current maximum did not occur at a potential that would overlap with the oxidation peak of the chloride ion.

For comparison purposes, a cyclic voltammogram was obtained for **2** without added dppm, (see Figure 3B). The well-defined reduction peak occurs at −2.03 V (g), similar to that reported for the electrochemical reduction of $PtCl_2(PPh_3)_2$.[17] Comparing Figure 3A with Figure 3B shows that the addition of dppm to a solution of **2** produces a platinum complex which is not **2**. ^{31}P NMR data substantiate that $[Pt(dppm)_2]Cl_2$ (**7**) forms, producing the wave at −1.16 V in Figure 3A.

Table II. Peak Potentials Measured in a 0.1 M TBAP Solution of Acetonitrile by Using an $Ag/AgNO_3$ Reference Electrode

complex	pot., V	figure, peak
$Pt_2Cl_2(dppm)_2$ (**1**)	−1.84	1, e
$PtCl_2(dppm)$ (**2**)	−2.03	3, g
$Pt_2(dppm)_3$ (**3**)	−0.76	
$[Pt_2Cl(\mu\text{-dppm})_2(\eta^1\text{-dppm})]Cl$ (**5**)	−1.64	1, a
$[Pt(dppm)_2]Cl$ (**7**)	−1.16	3, a
$[Pt_2(\mu\text{-dppm})_2(\eta^1\text{-dppm})_2]Cl_2$ (**6**)	−1.52	1, d
$[Pt_2H(\mu\text{-dppm})_2(\eta^1\text{-dppm})]Cl$ (**8**)	−1.93	1, b
$[Pt_2H_3(\mu\text{-dppm})_3]$ (**9**)	−2.07	1, c

Electrochemical Synthesis of 3 from 1 and 2. Controlled-potential electrolysis of **1** at −2.25 V produced a dark red precipitate at the surface of the mercury-pool electrode. After 4 h of electrolysis, the solution was carefully removed by syringe from the red precipitate of **3** (^{31}P NMR identification, 40% yield). This is the first electrochemical synthsis reported of a Pt(0) species that does not require trapping molecules for isolation and does not involve an additional step to separate the electrolyte from the product.

After electrolysis, the cyclic voltammogram revealed an oxidation peak at −0.76 V, where **3** was found to oxidize in a separate CV experiment, and a quasi-reversible oxidation–reduction wave at −0.32 and −0.44 V due to the presence of chloride ion.

Electrolysis of a solution of **2** and dppm at −2.35 V produced a red precipitate, which was isolated and identified as **3** as described previously. A cyclic voltammogram at the end of the electrolysis showed the presence of free chloride ions and a peak due to the oxidation of **3**. Some **4** was also present as in the chemical reduction of **2** with sodium.

Discussion

The chemical synthesis of **3** proceeded smoothly when either **1** or **2** was used. In the case of **2**, the isolated product contained a minor amount of **4**, which results from ligand exchange occurring prior to reduction. Replacement of chloride by dppm in **2** has been reported by others.[18] The substitution of chloride ligand by dppm occurred in the electrochemical reactions as well.

The assignments of the current maxima in Figure 1A are based on the comparison between parts A and B and the identification of **5** by NMR spectroscopy. In addition, it is anticipated that a decrease in the electron density at the metal centers will result when a chloride ligand in **1** is replaced by dppm. This is especially true if the added dppm is cis to the other two phosphine ligands already present.[17] Thus **5** is expected to be reduced at a more positive potential than **1**. If both chloride ligands are replaced by dppm molecules, which will occupy positions cis to the bridging phosphines, the electron density on the metal atoms will be reduced even further. This means that **6** should be more easily reduced than **5**. The reduction peak potential assignments for each of these complexes are given in Table II. A separate synthesis of **5** and subsequent cyclic voltammetry experiment verified the assignment of the reduction peak potential of **5** as −1.64 V.

Although the exact mechanism for the reduction of **1** to produce **3** when excess dppm is present is not fully resolved by the present work, it is clear that **3** is not a result of a single-step two-electron reduction of **1** or of **5**. Instead, the process appears to involve an electron-transfer step followed by at least one chemical reaction before the second electron transfer takes place. One possible pathway that is suggested is shown in Scheme II. Once electrons have been added to **5**, the chloride ligand dissociates, forming an intermediate that will accept a proton because of its electron-rich

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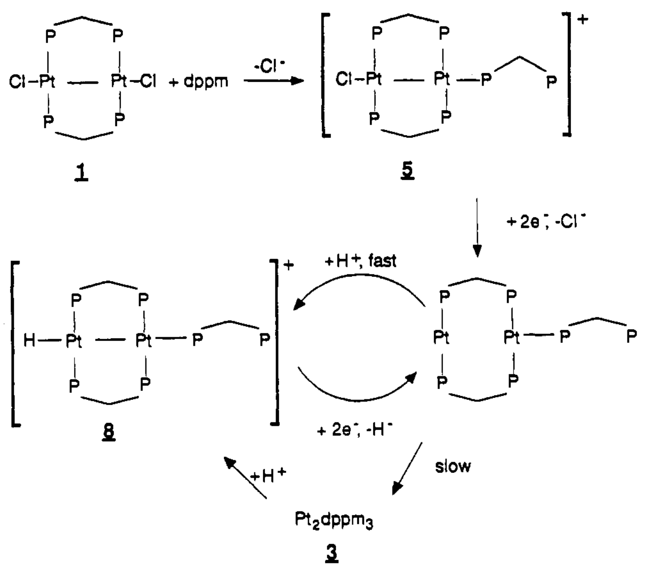
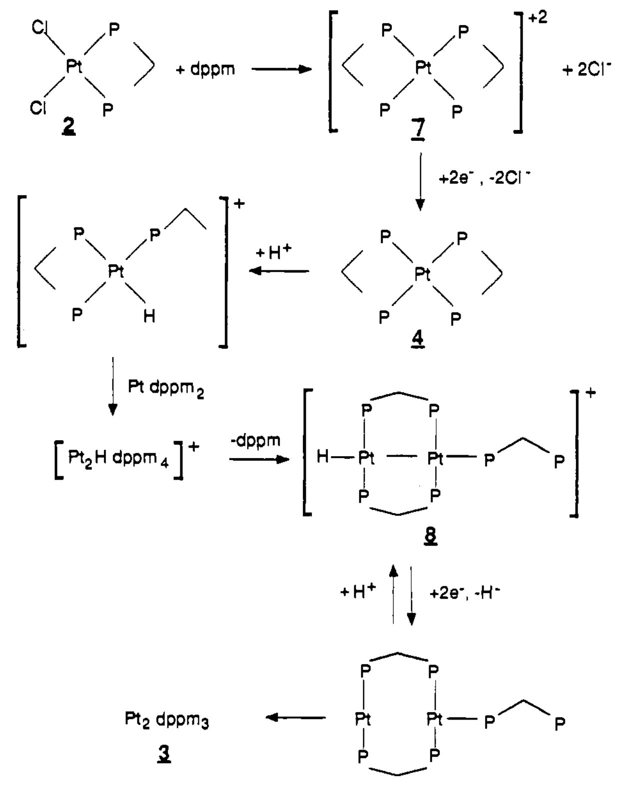
Scheme II



nature and available coordination site. This proton may come from the solvent or the electrolyte.[19] The product of this chemical process is the hydride complex $[Pt_2(\mu\text{-dppm})_2H(\eta^1\text{-dppm})]^+$ (**8**). Under the strong reducing conditions of the cell, **8** may give up a hydride, re-forming the intermediate. Cycling back and forth between **8** and the intermediate is possible. At the same time, some of the intermediate will go on to form **3** through the coordination of the dangling end of the third dppm ligand. Because **3** is a stable compound and its solubility in the cell solution is low, conversion back to the intermediate is unlikely. As a result, all of **5** eventually is converted into **3**.

The presence of **8** in the voltammogram shown in Figure 1A was confirmed by preparing a sample of **8** and measuring its reduction potential by cyclic voltammetry. Its reduction peak occurs at a potential of -1.93 V, which corresponds to peak b in Figure 1A. We also found that **3** will not form unless electrolysis takes place at a potential more negative than -2.07 V. Electrolysis at -1.80 V produced only a yellow solution. The cyclic voltammogram of this solution was identical with the one exhibited by a solution of **8**. In addition, we identified the presence of another hydride complex, $[Pt_2(\mu\text{-dppm})_2H_3]$ (**9**), in the cyclic voltammograms shown in Figure 1. The reduction peak for **9** occurs at -2.07 V. If **9** is also formed from the intermediate in Scheme II, it may then be converted to **8** by the addition of dppm.[11] Free dppm observed in the NMR spectrum is present in the solution during the entire reaction. We are continuing a more detailed investigation of the electrochemistry of these hydride complexes and will report our results in a subsequent paper. However it should be noted here that although loss of H_2 from **9** to form **8** was reported, loss of hydrogen from the monohydride **8** did not occur.[5,20] Our results indicate that, under electrolysis conditions where the applied potential is at least as negative as -2.15 V, loss of hydrogen from **8** does occur and the primary organometallic product is **3**.

Scheme III



Our results show that **2** also undergoes ligand substitution to form **7** before reduction takes place and that the reduction of **7** produces **3** when a large negative potential is applied. A possible reaction sequence for the electrochemical production of **3** from **2** is shown in Scheme III. In this sequence, reduction of **7** will produce **4**, which in turn participates in a chemical reaction to form a monohydride.[21] The monohydride complex may then react with **4**, producing the platinum hydride dimer **8**, by way of an intermediate that contains a five-coordinate platinum atom. A similar intermediate was detected when triphenylphosphine was used to induce reductive elimination of hydrogen from the binuclear platinum hydride **9**.[22] Further addition of electrons to **8** will lead to the formation of **3**. Comparing Figure 3A with Figure 1A shows that once electrons are added to either **5** or **7**, the chemical reaction that follows produces the same intermediates, since **8** and **9** are observed in both of these cyclic voltammograms. In addition, we have found that if electroysis is carried out at -1.51 V, just beyond the reduction potential observed for **7**, only a yellow solution forms. The cyclic voltammogram of this yellow solution is identical with that of a solution containing **8**. The ^{31}P NMR spectrum of this yellow solution confirmed the presence of the monohydride **8**. So even when **2** is used as the starting complex, the formation of **3** appears to be dependent upon the prior formation of **8**. Thus **3** is a result of the reduction of **8** and not **7**.

Conclusions

When chemical reduction is compared with electrochemical reduction, the results for **1** or **2** were found to be the same: The reduction of **1** by either method produces a high yield of **3** without contamination by other platinum complexes. A high yield of **3** was also obtained from **2** by either method, but the product has to be separated from **4**, which was also present at the end of each reaction. For a large-scale synthesis of **3**, the sodium reduction of **2** is the most rapid and the least costly method. However, for the production of small quantities of **3**, where no further purification would be necessary, the electrochemical reduction of **1** is clean and reliable.

The cyclic voltammetry and electrolysis experiments on **1** and **2** strongly suggest that the mechanism of these reactions is not a simple one-step reduction but may be an ece type mechanism. The platinum hydride complexes, **8** and **9**, are formed after the first electrons are transferred to **5** or **7**. It is these hydrides that lead to the formation of **3** when additional electrons are added. These results serve to emphasize the importance of platinum hydride complexes as intermediates in redox reactions and the desire of platinum to use hydrogen to fill vacant coordination sites. Because **8** and **9** are important for the formation of **3** when either **1** or **2** is used, the synthesis of Pt(0) dimers by these methods may be accomplished more readily from the direct use of platinum hydride complexes as starting materials.

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Intermediates in the 1,2-$(NH_2)_2C_6H_4$/$P(NEt_2)_3$ Transamination Reaction

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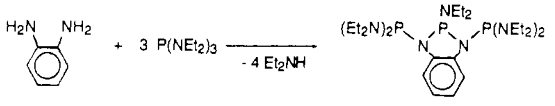
The diazaphosphole intermediates $C_6H_4(NH)_2PNEt_2$ (**2**), $C_6H_4(NH)P(NEt_2)NP(NEt_2)_2$ (**3**), and $[C_6H_4(NH)P(NEt_2)N][P(NH)_2C_6H_4]$ (**6**), the addition-coupled product of **2**, formed in the 1,2-$(NH_2)_2C_6H_4$/$P(NEt_2)_3$ transaminative formation of $C_6H_4[NP(NEt_2)_2]_2PNEt_2$ (**1**), have been characterized. Sulfur oxidation of P(III) product mixtures yields isolatable sulfides $C_6H_4(NH)_2P(S)NEt_2$ (**7**), $[C_6H_4(NH)_2P(S)][C_6H_4(NH)(N)P(S)NEt_2]$ (**8**), $C_6H_4(NH)PS(NEt_2)NPS(NEt_2)_2$ (**9**), and $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (**10**). **2**, **3**, and **6**–**10** are characterized by spectral data (MS, IR, and ^{31}P and ^1H NMR). **7**, **8**, and **10** are characterized by X-ray single-crystal analysis. **7**: monoclinic, $P2_1/c$, $a = 14.736$ (6) Å, $b = 8.872$ (5) Å, $c = 21.581$ (8) Å, $\beta = 104.38$ (3)°, $V = 2606$ (2) Å^3, $Z = 8$, $d_{calc} = 1.19$ g cm^{-3}. **8**: monoclinic, $P2_1/c$, $a = 21.384$ (9) Å, $b = 9.341$ (4) Å, $c = 22.293$ (8) Å, $\beta = 118.06$ (3)°, $V = 3930$ (3) Å^3, $Z = 8$, $d_{calc} = 1.38$ g cm^{-3}. **10**: triclinic, $P\bar{1}$, $a = 9.741$ (7) Å, $b = 11.655$ (5) Å, $c = 20.240$ (10) Å, $\alpha = 73.41$ (4)°, $\beta = 76.23$ (5)°, $\gamma = 79.17$ (5)°, $V = 2121$ (2) Å^3, $Z = 2$, $d_{calc} = 1.20$ g cm^{-3}. The **2** $\rightleftharpoons$ **6** equilibrium process and the oligomerization of **2** and **3** that occurs upon Et_2NH elimination have been examined. The role of 1,2- versus 1,4-transaminative addition in the coupling of **2** and **3** is discussed. Results are compared and contrasted with those of the $(Me_2N)_3P$/1,2-$(RNH)(NH_2)C_6H_4$ transamination reported recently. The reactions of **2** with Ph_2PCl and Et_3N yields tentatively characterized $C_6H_4(NPPh_2)_2PNEt_2$ (**11**); the reaction of **7** with Ph_2PCl and Et_3N forms the λ^3–λ^5–λ^3 mixed-valence triphosphazane $C_6H_4(NPPh_2)_2PSNEt_2$ (**13**).

Introduction

Synthesis of the skeletally stabilized triphosphazane **1** was reported recently from the transamination of 1,2-$(NH_2)_2C_6H_4$ with $P(NEt_2)_3$[2,3]. Formation of **1** is quantitative when excess $P(NEt_2)_3$ (>3:1) is used; however, at lower $P(NEt_2)_3$:1,2-$(NH_2)_2C_6H_4$ reactant ratios, tentative ^{31}P NMR spectral evidence for mono- (**2**) and diphosphazane (**3**) intermediates was obtained.[2b] This observation is of particular interest, since it contrasts earlier studies of $P(NMe_2)_3$/1,2-$(NH_2)(NHR)C_6H_4$ (R = H, Me, *i*-Pr) reactions by Malavaud and co-workers[4,5] in which only the cyclotetramers (**4**) and, at high temperatures, the phosphinimines (**5**) were observed. No evidence was reported for the presence of the monophosphorus analogue of **2**, which might precede **4**, or for two- or three-phosphorus intermediates between **4** and **5**. Thus, in order to better understand the $P(NR_2)_3$/1,2-$(NH_2)_2C_6H_4$ transamination reactions, we have studied the $P(NEt_2)_3$/1,2-$(NH_2)_2C_6H_4$ system in greater detail. We have isolated and characterized reaction intermediates and studied their elimination and subsequent condensation chemistry. The results of our work are reported below.



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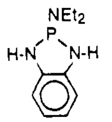

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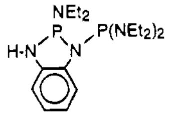

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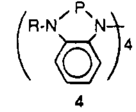

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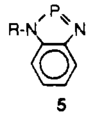

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Table I. Reactions of 1,2-$(NH_2)_2C_6H_4$ with $(Et_2N)_3P$

$(Et_2N)_3P$: 1,2-$(NH_2)_2C_6H_4$[b]	time, h[a]	amt of product, mol %[c]			
		$(Et_2N)_3P$	**2**	**3**	**1**
0.5:1	140 (45 °C)	37	16	3	
0.8:1	24 (60 °C)	0	80[d]	0	0
2:1	1.5	33	15	47	5
4:1	1.5	79	0	16	5
2:1	2.5	25	15	54	7
3:1	2.5	68	2	22	7
4:1	2.5	77	0	15	8
2:1	4	19	21	52	8
4:1	4	73	0	14	13
2:1	9	7	23	54	16

[a] All reactions at 85 °C except as noted. [b] Mole ratios. [c] Determined from ^{31}P NMR spectral areas. [d] 20% of the reaction mixture was due to compound **6**.

Experimental Section

Apparatus and Materials. Phosphorus-31 NMR spectra were recorded with JEOL FX-90Q and Bruker WM-250 spectrometers at 36.5 and 101.2 MHz, respectively. ^1H NMR spectra were obtained on a JEOL FX-90Q spectrometer at 90 MHz or a Varian Gemini-300 NMR spectrometer at 300 MHz. ^{31}P and ^1H chemical shifts downfield from 85% H_3PO_4 (external) and Me_4Si (internal) are reported as positive (+δ). IR spectra (4000–400 cm^{-1}) were obtained on a Beckman 4250 or IBM IR/32 Type 9132 spectrometer. Mass spectra were obtained at 70 eV with a Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometer. Mass spectral data refer to the major peak of the respective envelope. Chemical ionization (CI$^+$ and CI$^-$) was achieved with isobutane as the ionizing gas. Exact mass analyses were referenced to perfluorokerosene. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochromator and low-tem-

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