according to

$$4Cu(II) + 5MIBA \rightarrow Cu^{I}_{2}Cu^{II}_{2}(MIBA)_{3} + MIBA(SS)$$

$$5Cu(I) + {}^{3}\!/_{2}MIBA(SS) \rightarrow Cu^{I}_{2}Cu^{II}_{2}(MIBA)_{3} + Cu(II)$$

The copper(II):MIBA ratio of 4:5 corresponds to a 0.44 predicted optimum ratio on the copper(II) plus MIBA Job's plot (*A*), and the copper(I):MIBA(SS) ratio of 10:3 corresponds to a 0.77 predicted optimum ratio on the copper(I) plus MIBA(SS) Job's plot (*C*). If the 1 mol of MIBA(SS) liberated as the oxidation product in the first reaction is fully converted to colored complex by the addition of excess copper(I), the color intensity should increase 67% corresponding to the formation of an additional 0.67 mol of colored product (*B*). If the 1 mol of copper(II) formed as oxidation product in the second reaction is converted to colored complex by the addition of excess MIBA, the color intensity should increase 25% in accordance with the formation of 0.25 mol of colored product (*D*). $Cu^{I}_{2}Cu^{II}_{2}(MIBA)_{3}$ thus represents the best fit of the spectral parameters by predicting values which fall within the experimentally observed range in three of the four categories. The one category (*D*) out of four which does not show agreement between theory and observation involves absorbance intensification of the copper(I) plus MIBA(SS) product. This discrepancy may be resolved if some of the CuCl reactant has been oxidized prior to the formation of the purple complex. The reaction between CuCl and MIBA(SS) was slow because of the limited solubility of both MIBA(SS) and CuCl in aqueous solution. Therefore, a small amount of atmospheric oxidation could have taken place under the conditions of the reaction. Additionally, there was a trace of a copper(II) impurity in the CuCl. The preceding assumption is consistent with the observed extinction coefficient of the solution corresponding to the optimum point on the copper(I) plus MIBA(SS) Job's plot. The extinction coefficient of this solution was predicted to be 1200 and was expected to increase to the full 1500 value upon addition of excess MIBA. In actuality, the optimum solution only had an ϵ_{max} of 1000 but it increased to the expected value of 1500 in the presence of excess MIBA. This suggests that there was sufficient copper present to lead ultimately to full color development, but there was insufficient copper(I) to yield the predicted absorbance with MIBA(SS). The predicted Job's plot optimum value (*C*) is still within the experimentally observed range if calculated on the basis of the proposed prior oxidation of less than 10% of the CuCl. The precipitated complex contains water and the stoichiometry $Cu^{I}_{2}Cu^{II}_{2}(MIBA)_{3}\cdot 4H_{2}O$ approximates the analytical data obtained for the solid species except that it does not account for the presence of small quantities of chloride. An experimental molecular weight of 790 in H_2O is rather close to the predicted value of 680.

Returning to the penicillamine system, we suggest that the observed complications are primarily due to polymerization, to the inhibition of the reaction by penicillamine disulfide, and to the unusual role of chloride (and bromide) which is still unexplained.

Acknowledgment. We wish to thank the NSF for support of this research.

Registry No. Penicillamine, 52-67-5; MIBA, 4695-31-2; MIBA(SS), 4695-30-1; Cu, 7440-50-8.

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Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Interconversion Reactions between Substituted Phosphinous Acid–Phosphinito Complexes of Platinum(II) and Their Capping Reactions with Boron Trifluoride–Diethyl Etherate

William B. Beaulieu, Thomas B. Rauchfuss,
and D. Max Roundhill*

Received January 2, 1975 AIC50008B

Recently a number of workers have prepared transition metal complexes of substituted phosphinites and secondary phosphites. The ligands, however, tend to be hydrolytically unstable and the complex obtained contains the coordinated resulting acid and its conjugate base. In earlier work we had found that alkyl diphenylphosphinite complexes of platinum would undergo hydrolysis to give complexes containing coordinated diphenylphosphinous acid and diphenyphosphinite[1] groups.[2,3] From the hydrolysis of $Pt(ROPPh_2)_4$ [R = Me, *n*-Bu] the three complexes $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$, $PtH(OPPh_2)(HOPPh_2)_2$, and $Pt(OPPh_2)_2(HOPPh_2)_2$ were obtained. In a separate study Dixon et al. prepared $Pt(OPPh_2)_2(HOPPh_2)_2$ by treating $PtCl(OPPh_2)(HOPPh_2)_2$ with $AgOPPh_2$.[4] Dixon postulated that the hydrogen atoms on the diphenylphosphinous acid groups were symmetrically H bonded between the diphenylphosphinito and diphenylphosphinous acid moieties. This idea was implicitly understood in our second publication,[2] and more recently a communication on the single-crystal X-ray structure determination of the compound $Pd_2(SCN)_2[(OPPh_2)_2H]_2$[5] has given further credence to this claim. This bifunctional hydrogen-bonded ligand structurally resembles the anion in $[PtH(PPh_3)_3](CF_3CO_2)_2H$.[6]

The hydrolysis of chlorodiphenylphosphine,[7] trialkyl phosphite,[8,9] or alkyl diphenylphosphinite[1,2] complexes of platinum leads to phosphorus-bonded complexes of this hydrogen-bonded six-membered ring system. Since these phosphorus compounds undergo more facile hydrolysis when they are not coordinated to a transition metal,[10] it appears likely that these synthetic routes involve the acid as the reactive species.[9] A recent communication has indicated that the salts of these acids are not widely recognized as ligands,[11] but in this note we will present compelling evidence that the formation of diphenylphosphinous acid–diphenylphosphinito complexes of Pt^{II} by the hydrolysis route involves the intermediacy of diphenylphosphinous acid as the reactant.

Results and Discussion

The hydrazine reduction of a suspension of $PtCl_2(n\text{-}BuOPPh_2)_2$ in aqueous ethanol and $n\text{-}BuOPPh_2$ leads to the formation of $Pt(n\text{-}BuOPPh_2)_4$.[1] This product must be quickly separated from the reaction medium, however, or subsequent hydrolysis occurs leading to the formation of either $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ or $Pt(OPPh_2)_2(HOPPh_2)_2$. When $Pt(MeOPPh_2)_3$ is allowed to hydrolyze under similar conditions, the product is $PtH(OPPh_2)(HOPPh_2)_2$.[2] These products undoubtedly arise from the facile hydrolysis of the respective alkyl diphenylphosphinites. The initially formed Pt(0) complex is kinetically labile, and the free alkyl diphenylphosphinite in solution can hydrolyze to diphenylphosphinous acid. The diphenylphosphinous acid formed can either coordinate to the zerovalent platinum as a donor, or it can add the P–H bond to form a hydroplatinum(II) complex. This explanation would rationalize the formation of both $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ and $PtH(OPPh_2)(HOPPh_2)_2$. The former can be isolated from the reaction medium since the partially hydrolyzed complex is now kinetically inert, and in addition its isolation is favored since it precipitates from the reaction medium. If these compounds are formed by successive hydrolysis of the alkyl diphenylphosphinite, we should be able to convert $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ into $PtH(OPPh_2)(HOPPh_2)_2$. This has now been effected by refluxing in aqueous butanol, eq 1.

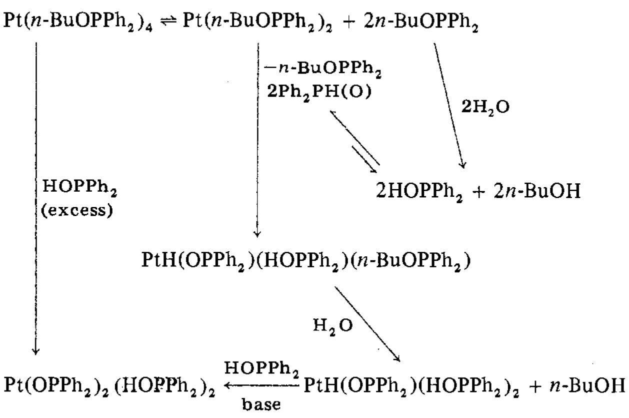
$$PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2) + H_2O \rightarrow PtH(OPPh_2)(HOPPh_2)_2 + n\text{-}BuOH \qquad (1)$$

We have also found that the transformation of $PtH(OPPh_2)(HOPPh_2)_2$ into $Pt(OPPh_2)_2(HOPPh_2)_2$ can be effected by refluxing $PtH(OPPh_2)(HOPPh_2)_2$ with $HOPPh_2$ in aqueous ethanol as solvent in the presence of a base, eq 2.

$$PtH(OPPh_2)(HOPPh_2)_2 + HOPPh_2 \rightarrow Pt(OPPh_2)_2(HOPPh_2)_2 + H_2 \qquad (2)$$

In the presence of excess $HOPPh_2$ it is possible to convert $Pt(n\text{-}BuOPPh_2)_4$ into $Pt(OPPh_2)_2(HOPPh_2)_2$ without the intermediate formation of the hydrido complexes. These transformations are shown in Scheme I.

Scheme I



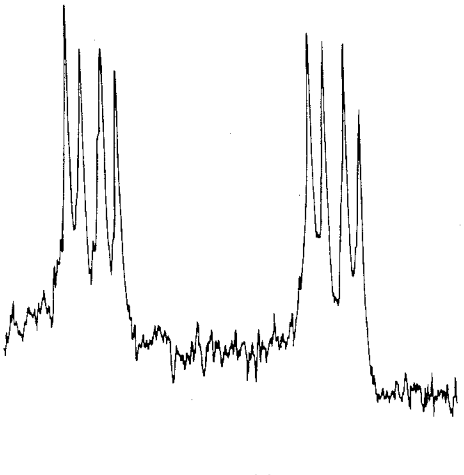
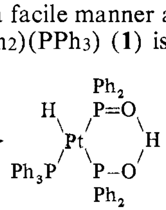


Figure 1.

The protonation by $HOPPh_2$ (or as the tautomeric form $Ph_2PH(O)$) remains the speculative aspect of this reaction scheme. In order to verify the plausibility of this step we have treated $Pt(PPh_3)_4$ with a slight excess of $HOPPh_2$. The addition proceeds in a facile manner at room temperature as $PtH(OPPh_2)(HOPPh_2)(PPh_3)$ (**1**) is obtained, eq 3. [Al-

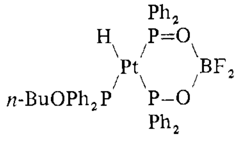
$Pt(PPh_3)_4 + 2HOPPh_2 \rightarrow$  $+ 3PPh_3$ (3)

1

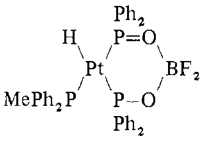
though the structures shown depict the diphenylphosphinous acid–diphenylphosphinito complexes as valence-bond structures, we recognize the likelihood that the conjugated ring structure representation is equally appropriate.] This product is unusual in that the anticipated stoichiometry of the product of addition of HX to $Pt(PPh_3)_4$ is $PtHX(PPh_3)_2$.[12] A similar reaction pattern has been observed on treating $Pt(PPh_3)_4$ with 2-(methylthio)ethanethiol, when the product is $PtH(SCH_2CH_2SMe)(PPh_3)$.[13] This difference in stoichiometry of the product in the HX addition has been ascribed to the chelate-assisted addition of the polyfunctional addend causing an additional triphenylphosphine to be displaced. The similarity in reaction patterns may be a consequence of diphenylphosphinous acid, in its diphenylphosphine oxide tautomeric form, existing as a dimer[14] in solvents of low dielectric constant such as benzene. An alternative explanation, however, is that the initial product is $PtH(OPPh_2)(PPh_3)_2$ and that the driving force to the displacement of the further PPh_3 molecule by diphenylphosphinous acid is the formation of the hydrogen-bonded ring structure. Compound **1** is insoluble in common organic solvents, but the analogous complex $PtH(OPPh_2)(HOPPh_2)(PMePh_2)$ (**2**), which can be obtained by treating $Pt(PMePh_2)_4$ with $HOPPh_2$, is quite soluble. The ^1H NMR spectrum of complex **2** in the high-field region is shown in Figure 1. The resonance is centered at τ 13.91 with $J_{P(trans)\text{-}H} = 166$ Hz and $J_{P(cis)\text{-}H} = 24$ and 10 Hz, respectively. This spectrum closely resembles that for $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ which has the resonance centered at τ 14.14 with $J_{P(trans)\text{-}H} = 157$ Hz and $J_{P(cis)\text{-}H} = 26$ and 12 Hz, respectively. The value of $J_{P(cis)\text{-}H} = 26$ Hz is considerably larger than expected for coupling with $PMePh_2$[12] and so we consider it likely that this coupling is due to the *cis*-diphenylphosphinito group. The values of $J_{Pt\text{-}H}$ are 880 and 884 Hz for $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ and $PtH(OPPh_2)(HOPPh_2)(PMePh_2)$, respectively.

The methyl resonance (τ 8.55) appears as two doublets separated by 9 Hz. This resonance is anticipated to be a complex pattern since the $PMePh_2$ group is both cis and trans to a coordinated phosphorus, and the possibility of virtual coupling leads to the prediction of some multiplicity. The acid hydrogen on the coordinated diphenylphosphinous acid is broad ($\sim$22 Hz) and centered at τ −3.43. Because of the low solubility previous workers[2,4] were unable to observe this resonance in $Pt(OPPh_2)_2(HOPPh_2)_2$.[2,15]

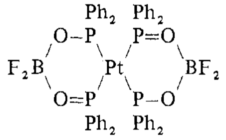
The ring hydrogen atom can be readily replaced with $-BF_2$ by treating the compounds with $BF_3 \cdot Et_2O$. From this reaction we have prepared the capped compounds **3**–**5**. Compound **4**



3



4



5

is quite soluble in organic solvents and the ^{1}H NMR spectrum of the complex in the upfield region shows a similar multiplicity to that of **2**. The resonance of **4** is centered at τ 13.55 which represents a shift of 36 Hz from the position of the resonance in compound **2**. The infrared spectra of complexes **3**–**5** show $\nu_{\text{B-F}}$ in the range 1000–1050 cm^{-1}.

Experimental Section

Infrared spectra were obtained as Nujol mulls on Perkin-Elmer Model 700 and 457 spectrometers. ^{1}H NMR spectra were obtained at 100 MHz on Varian HA 100 or at 60 MHz on Varian T-60 spectrometers. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Diphenylphosphinous acid was prepared by the hydrolysis of chlorodiphenylphosphine and subsequently purified.[16] Reactions were carried out in a nitrogen atmosphere. Microanalyses were carried out on a Perkin-Elmer Model 240 elemental analyzer except for fluorine analyses which were carried out by Galbraith Laboratories, Inc.

Hydridodiphenylphosphinito(diphenylphosphinous acid)triphenylphosphineplatinum(II), 1. To a solution of $Pt(PPh_3)_4$[17] (300 mg) in dry benzene (10 ml) was added diphenylphosphinous acid until the orange color disappeared. The solvent was removed and ether added to give the complex as a colorless precipitate, 161 mg (72%); mp 196–200°. Anal. Calcd for $C_{42}H_{37}O_2P_3Pt$: C, 58.5; H, 4.30. Found: C, 58.8; H, 4.34.

Hydridodiphenylphosphinito(diphenylphosphinous acid)methyldiphenylphosphineplatinum(II), 2. To a solution of $Pt(PMePh_2)_4$[18] (767 mg) in oxygen-free benzene was added diphenylphosphinous acid until the orange color of the solution disappeared. After stirring for 1 hr, the solution was dried with $MgSO_4$. After 15 min the solvent was removed and ether added to give the complex as colorless crystals, 544 mg (88%); mp 185–187°. Anal. Calcd for $C_{37}H_{35}O_2P_3Pt$: C, 55.6; H, 4.38. Found: C, 55.9; H, 4.34.

Hydridodiphenylphosphinito(difluoroboron diphenylphosphinite)(*n*-butyl diphenylphosphinite)platinum(II), 3. To $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ (200 mg) in dry ether (7 ml) was added $BF_3\cdot Et_2O$ (3 drops). After 3 hr of stirring the complex was filtered and recrystallized from CH_2Cl_2 and ether, 187 mg (89%); mp 155–158°. Anal. Calcd for $C_{40}H_{40}BF_2O_3P_3Pt$: C, 53.0; H, 4.42; F, 4.20. Found: C, 53.4; H, 4.33; F, 4.28.

Hydridodiphenylphosphinito(difluoroboron diphenylphosphinite)methyldiphenylphosphineplatinum(II), 4. To a solution of $PtH(OPPh_2)(HOPPh_2)(PMePh_2)$ (100 mg) in dry ether (7 ml) was added $BF_3\cdot Et_2O$ (5 drops). After 4 hr of stirring the colorless precipitate was filtered and recrystallized from CH_2Cl_2 and hexane, 86 mg (81%); mp 179–181°. Anal. Calcd for $C_{37}H_{34}BF_2O_2P_3Pt$: C, 52.4; H, 4.01; F, 4.49. Found: C, 52.2; H, 4.10; F, 4.59.

Bis(diphenylphosphinito)bis(difluoroboron diphenylphosphinite)platinum(II), 5. To a solution of $Pt(OPPh_2)_2(HOPPh_2)_2$ (100 mg) in dry ether (7 ml) was added $BF_3\cdot Et_2O$ (5 drops). After 4 hr of stirring the light yellow color of the solution was discharged and a white precipitate obtained. The compound was filtered and washed with ether, 78 mg (71%); mp 300°. Anal. Calcd for $C_{48}H_{40}B_2F_4O_4P_4Pt$: C, 52.5; H, 3.65; F, 6.93. Found: C, 52.8; H, 3.65; F, 7.15.

Conversion of $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ into $PtH(OPPh_2)(HOPPh_2)_2$. To aqueous *n*-butyl alcohol was added $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$ (280 mg) and the mixture was refluxed for 2 hr. The resulting precipitate, $PtH(OPPh_2)(HOPPh_2)_2$, was filtered and washed consecutively with water and ether, 139 mg (63%).

Conversion of $PtH(OPPh_2)(HOPPh_2)_2$ into $Pt(OPPh_2)_2(HOPPh_2)_2$. To a suspension of $PtH(OPPh_2)(HOPPh_2)_2$ (200 mg) in ethanol (14 ml) was added diphenylphosphinous acid (300 mg). To the stirred mixture was added hydrazine (5 drops of 85%) when the color became pale yellow. After 4 hr, further hydrazine (20 drops) was added and the mixture stirred for 12 hr. The solvent was removed to leave a yellow oil. Addition of ether gave a compound which was recrystallized from CH_2Cl_2 and ether, 99 mg (40%).

Conversion of $Pt(n\text{-}BuOPPh_2)_4$ into $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$. To a solution of ethanol (7 ml) and water (3 ml) was added $Pt(n\text{-}BuOPPh_2)_4$ (100 mg). The solution was refluxed and $HOPPh_2$ (~10–15 mg) added. After 12 hr the solution was colorless. Upon cooling, the complex was obtained in quantitative yield.

Conversion of $Pt(n\text{-}BuOPPh_2)_4$ into $PtH(OPPh_2)(HOPPh_2)_2$. To a stirred solution of $Pt(n\text{-}BuOPPh_2)_4$ in dry benzene was added $HOPPh_2$ until the orange color was discharged. After 30 min the solvent was removed to leave an oil. Trituration with ethanol (6 ml) and water (2 ml) followed by refluxing gave a white precipitate.

Conversion of $Pt(n\text{-}BuOPPh_2)_4$ into $Pt(OPPh_2)_2(HOPPh_2)_2$. An analogous procedure was used as for the conversion into $PtH(OPPh_2)(HOPPh_2)_2$ except that the solution was refluxed for 1 hr; the yield of product was high.

Acknowledgment. We wish to thank the University of Idaho and Imperial College, London, for the use of HA 100 NMR spectrometers. Thanks are due to the National Science Foundation for support under Grant No. GP-38775.

Registry No. 1, 55012-57-2; **2**, 55012-58-3; **3**, 55012-59-4; **4**, 55012-60-7; **5**, 55012-61-8; $Pt(PPh_3)_4$, 14221-02-4; $HOPPh_2$, 24630-80-6; $Pt(PMePh_2)_4$, 27121-53-5; $PtH(OPPh_2)(HOPPh_2)(n\text{-}BuOPPh_2)$, 55056-98-9; $BF_3\cdot Et_2O$, 109-63-7; $Pt(OPPh_2)_2(HOPPh_2)_2$, 36488-71-8; $PtH(OPPh_2)(HOPPh_2)_2$, 55056-99-0; $Pt(n\text{-}BuOPPh_2)_4$, 36472-78-3.

References and Notes

(1) Previously the term "diphenylphosphinate" has been used to identify P-bonded complexes of Ph_2PO^-. This nomenclature, however, fails to discriminate these complexes from those derived from $Ph_2PO_2^-$, which have also been termed "diphenylphosphinato" complexes [H. D. Gillman, P. Nannelli, and B. P. Block, *J. Inorg. Nucl. Chem.*, **35**, 4053 (1973)]. In order to distinguish between these two sets of distinctly different types of complexes, we propose the use of the term "diphenylphosphinite" for the P-bonded compounds.

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