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Reactions of Nitrosonium Salts with Complexes of Platinum

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Reactions of nitrosonium salts with the complexes $M(\text{PPh}_3)_2\text{O}_2$ ($M = \text{Pt}$ and Pd) result in the formation of $[M(\text{PPh}_3)_2(\text{NO}_3)]^+$ in acetonitrile and of the hydroxy-bridged dimers $[M_2(\text{PPh}_3)_4(\text{OH})_2]^{2+}$ in less basic solvents containing traces of water. The reactions of nitrosonium salts with platinum(0) complexes give cationic platinum(II) species $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]^{2+}$ and $[\text{Pt}(\text{PPh}_3)_3]^{2+}$.

Introduction

Metal-catalyzed reactions of dioxygen have attracted considerable recent attention, with primary focus on metal-dioxygen complexes which have been isolated and characterized.² Among the few reactions of these complexes with simple inorganic substrates which have been reported³ are the reactions of NO and NO_2 which yield nitrito and nitrate metal complexes. We were interested in studying the reaction of the nitrosonium cation (NO^+) with $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ for two reasons: (1) since CO reacts with $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ to form the bidentate carbonato complex,⁴ the isoelectronic NO^+ might be expected to form the bidentate nitrate complex $[\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)]^+$; (2) the nitrosonium cation might be expected to react with the metal-dioxygen compound as a strong electrophile such as H^+ , PhCO^+ , or Ph_3C^+ , which give the corresponding peroxides.^{5,6}

Since oxidative addition reactions of the electrophiles H^+ and RN_2^+ with $\text{Pt}(\text{PPh}_3)_3$ have previously been reported,^{7,8} it was of interest to study the reaction of NO^+ with platinum(0) compounds. Since nitrosyl complexes of Ru ,⁹ Rh ,¹⁰ and Ir ¹¹ are readily formed by reactions of NO^+ , it was of interest to probe NO^+ reactions as an entry into the ill-defined area of nitrosyl-platinum-triphenylphosphine systems.

Results and Discussion

The reaction of NOBF_4 and $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ in acetonitrile gave $[\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)][\text{BF}_4]$, a 1:1 electrolyte in nitromethane. This compound was characterized by elemental analysis, a ^1H NMR spectrum which shows only the presence of triphenylphosphine protons at τ 2.85, and nitrate infrared frequencies in KBr at 1490, 1260, and 970 cm^{-1} . These frequencies are in the region observed for symmetrical bidentate nitrate metal complexes.¹² Upon prolonged standing in solvents such as chloroform or dichloromethane, decomposition of the nitrate compound to the dimer $[\text{Pt}_2(\text{PPh}_3)_4(\text{OH})_2][\text{BF}_4]_2$ (vide infra) was observed.

In less basic and more poorly coordinating solvents such as chloroform, dichloromethane, benzene, or nitromethane the primary product (more than 50%) formed in the reaction of $M(\text{PPh}_3)_2\text{O}_2$ and NOX ($M = \text{Pt}$ and Pd ; $X = \text{BF}_4$ and PF_6) was the hydroxy-bridged dimer $[M_2(\text{PPh}_3)_4(\text{OH})_2]X_2$, while the nitrate complex $M(\text{PPh}_3)_2(\text{NO}_3)$ ¹³ was formed in variable yields. These products were obtained even in experimental runs where stringent precautions (including baking of glassware and distillation of solvents under dry nitrogen) were taken to exclude water.

The hydroxy-bridged dimer has been reported in the reaction of oxygen with methanolic suspensions of $[\text{Pt}(\text{PPh}_3)_3(\text{NCC}_6\text{H}_4\text{R})][\text{BF}_4]$ ⁸ and in the reaction of $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ with AgBF_4 in moist acetone.¹⁴ To elucidate the course of the reaction which leads to the formation of the hydroxy dimer from $M(\text{PPh}_3)_2\text{O}_2$ and NOX , the following experiments were performed.

(1) The reaction of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ and NOBF_4 in CDCl_3 and in C_6D_6 gave no significant absorption in the 2620-cm^{-1} region where the deuterated hydroxy dimer $[\text{Pt}_2(\text{PPh}_3)_4(\text{OD})_2]^{2+}$ absorbs.¹⁴

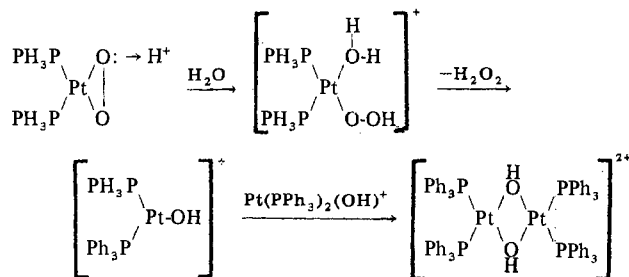
(2) The addition of 0.02 ml of D_2O in 5.0 ml of chloroform to solid $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ and NOBF_4 gave a product which had $\nu(\text{O-H})$ at 3550 cm^{-1} and $\nu(\text{O-D})$ at 2620 cm^{-1} of approximately equal intensities. The addition of solvent containing more D_2O (0.20 ml in 5.0 ml of CHCl_3) led to a product with a $\nu(\text{O-D})$ band considerably more intense than the $\nu(\text{O-H})$ band. Exchange of H-D in the hydroxy dimer is slow and requires a catalyst.¹⁴

(3) The reaction of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ in chloroform with aqueous 48% tetrafluoroboric acid gave high yields of the dimer $[(\text{Pt}_2(\text{PPh}_3)_4(\text{OH})_2)[\text{BF}_4]_2]$.

(4) When several drops of D_2O were added to a mixture of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ and NOBF_4 in acetonitrile 1 min after mixing the reagents, no hydroxy-bridged dimer was formed.

(5) No reaction was observed when a solution of $[\text{PtH}(\text{PPh}_3)_3][\text{BF}_4]$ in chloroform was treated with oxygen for 1 hr. This experiment suggests that a metal hydride is not involved in the formation of the hydroxy dimer. Metal-hydroxy complexes are formed by the reaction of metal hydrides and dioxygen in other systems.¹⁵

On the basis of the above experiments it is reasonable to suggest that the formation of the hydroxy-bridged dimer proceeds by an ionic pathway involving a proton derived from traces of water (or alcohol) in the system. The failure to obtain deuterated products from the reactions in CDCl_3 and C_6D_6 appears to exclude a free-radical pathway such as has been observed in reactions of alkyl halides with platinum(0) compounds^{16a} or in oxidations using palladium(0) complexes.^{16b} The nitrosonium cation reacts rapidly with traces of water (or alcohol) in the system to give H^+ and HONO (or RONO). Formation of the hydroxy dimer may then proceed as follows:



The formation of hydrogen peroxide in reactions of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ has previously been reported.⁵ The presence of $\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)_2$ in some cases may be due to the reaction of NO^+ (before hydrolysis), first giving the nitrate complex obtained in the reaction in acetonitrile, described above, followed by intermolecular substitution reactions which give the dinitrate and $\text{Pt}(\text{PPh}_3)_2^{2+}$, the precursor of the hydroxy-bridged dimer.

Reactions of Complexes of Platinum(0) with NOBF_4 . The reaction of $\text{Pt}(\text{PPh}_3)_3$ with NOBF_4 in solvents such as chloroform, dichloromethane, benzene, and nitromethane gave red or brown products whose infrared spectra show bands

characteristic only of triphenylphosphine and the tetrafluoroborate anion. In many trials infrared bands at 720 and 1120 cm^{-1} , possibly due to the presence of coordinated triphenylphosphine oxide, were observed. On occasion some free triphenylphosphine oxide, characterized by a strong absorption at 1190 cm^{-1} in the infrared, was obtained.¹⁷ The reaction of $\text{Pt}(\text{PPh}_3)_4$ and NOBF_4 gave similar products, except that a considerable quantity of free triphenylphosphine oxide was always obtained.

The reaction of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with 2 mol of NOBF_4 in acetonitrile gave $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$, a 2:1 electrolyte in nitromethane. This white salt was characterized by elemental analysis, ir spectra, and a ^1H NMR spectrum in which the phenyl proton resonances at τ 2.5 and 2.6 have an integrated area approximately five times that of the methyl (acetonitrile) resonance at τ 8.4. This compound, like a few other acetonitrile complexes, has a very weak band in the 2300- cm^{-1} region assigned to the $\text{C}\equiv\text{N}$ stretching frequency. $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]^{2+}$ is similar to the dicationic diolefinic complexes $[\text{M}(\text{diolefin})(\text{CH}_3\text{CN})_2]^{2+}$ of Pt(II) and Pd(II) recently reported by Roulet and Vouillamoz.¹⁸ Treatment of $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$ with an excess of triphenylphosphine gave $[\text{Pt}(\text{PPh}_3)_3][\text{BF}_4]_2$, a 2:1 electrolyte in nitromethane. This compound was characterized by elemental analysis and a ^1H NMR spectrum which shows a peak at τ 2.70 with an integrated area twice that of a pair of peaks at τ 2.90 and 3.07. The compound has an ir spectrum which is quite similar to those obtained for products of the $\text{Pt}(\text{PPh}_3)_3\text{-NOBF}_4$ reaction described earlier, except that in this case no triphenylphosphine oxide is present.

The formation of a complex formulated as $\text{Pt}(\text{PPh}_3)_3^{2+}$ is somewhat surprising, since d^8 platinum(II) complexes are almost invariably four coordinate. One possible suggestion for the structure of $\text{Pt}(\text{PPh}_3)_3^{2+}$ is that one of the triphenylphosphine ligands is π bonded to the metal through a phenyl group as in complexes in which a tertiary phosphine coordinates in a η^6 fashion through an aryl substituent. These complexes include $\text{Mo}(\text{PMe}_2\text{Ph})_3(\eta\text{-PhPMe}_2)^{19a}$ and $\text{RuH}(\text{PPh}_3)_2(\eta\text{-PhPPH}_2)^+.$ ^{19b,c} The structure of $\text{Pt}(\text{PPh}_3)_3^{2+}$ would then be similar to that of $[(\eta^5\text{-C}_5\text{H}_5)\text{Pt}(\text{PPh}_3)_2]^+$ cation, in which a platinum atom with two triphenylphosphine ligands is bonded to a delocalized 6 π -electron system.²⁰ Another possible formulation for the compound is $[\text{Pt}(\text{PPh}_3)_3(\text{H}_2\text{O})]^{2+}$, which would be analogous to the $[\text{Pd}(\text{PPh}_3)_3(\text{H}_2\text{O})]^{2+}$ reported previously,⁷ but the ir spectrum of the tris(triphenylphosphine)platinum cation has only a very weak absorption band at 3400 cm^{-1} and no ir bands which may be ascribed to OH deformation modes.

The nitrogen-containing product resulting from the reduction of the nitrosonium ion in its reactions with platinum(0) compounds was nitrous oxide (ir absorption at 2210 cm^{-1}). During the early stages of these reactions nitric oxide (ir absorption centered at 1880 cm^{-1}) was also detected. There was no indication of the formation of the hyponitrite complex $\text{Pt}(\text{PPh}_3)_2\text{N}_2\text{O}_2$ which is formed in the reaction of NO with $\text{Pt}(\text{PPh}_3)_3.$ ²¹ The detection of nitric oxide, the one-electron reduction product of the nitrosonium ion, augments the recent finding of one-electron reduction products in reactions of platinum(0) complexes with one-electron acceptors.²² The formation of triphenylphosphine oxide in reactions of NOBF_4 with $\text{Pt}(\text{PPh}_3)_3$ must be due to the reaction of nitric oxide and triphenylphosphine.²³

Experimental Section

The starting materials $\text{Pt}(\text{PPh}_3)_4,$ ²⁴ $\text{Pt}(\text{PPh}_3)_3,$ ²⁴ $\text{Pt}(\text{PPh}_3)_2\text{O}_2,$ ²⁵ $\text{Pd}(\text{PPh}_3)_2\text{O}_2,$ ²⁵ $[\text{PtH}(\text{PPh}_3)_3][\text{BF}_4],$ ⁷ and $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ ²⁶ were prepared by methods previously described. Nitrosonium tetrafluoroborate and hexafluorophosphate (Alfa) were purified by vacuum sublimation or dried in vacuo and stored in a nitrogen atmosphere over P_2O_5 . Solid reagents were handled in a glove box under nitrogen.

Acetonitrile was distilled from P_2O_5 and stored under nitrogen. Chloroform and benzene were freshly distilled from CaCl_2 or passed through a column of alumina. Infrared spectra were recorded in KBr pellets or Nujol Mulls on Perkin-Elmer Models 621 or 457 spectrophotometers. Conductivity measurements were made with an Industrial Instruments Model RC 16B2 conductivity bridge. A Varian A-60 instrument was used to record the ^1H nuclear magnetic resonance spectra which were obtained in CDCl_3 or CH_2Cl_2 . Melting or decomposition points were obtained using a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. and Galbraith Laboratories, Inc., Knoxville, Tenn.

Nitratobis(triphenylphosphine)platinum(II) Tetrafluoroborate ($[\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)]_2[\text{BF}_4]$). When solid NOBF_4 (41 mg) was added to a suspension of 260 mg of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ in 5 ml of acetonitrile, a clear red solution was obtained in less than 1 min. The solvent was removed under reduced pressure and the residue was dissolved in chloroform. After filtration the chloroform was stripped in vacuo and the red solid was triturated with ether. Yield: 291 mg (97%). The compound began to decompose at 133°C. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_3\text{O}_3\text{PtBF}_4$: C, 49.8; H, 3.45; N, 1.61. Found: C, 48.2; H, 3.61; N, 1.66. Molar conductivity of 10^{-3} M nitromethane solution at 25°C, 100 $\text{ohm}^{-1}\text{cm}^2$.

Di- μ -hydroxo-tetrakis(triphenylphosphine)diplatinum(II) Tetrafluoroborate ($[\text{Pt}_2(\text{PPh}_3)_4(\text{OH})_2][\text{BF}_4]_2$). Method A. A solution of 288 mg of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ in 5 ml of chloroform was stirred under nitrogen with 44 mg of NOBF_4 . After 1 hr the reaction mixture was evaporated to dryness and triturated with ether to give 297 mg of a yellowish-tan solid. The solid was stirred with benzene and filtered (33 mg of $\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)_2$ was recovered from the filtrate). The residue was washed with 5 ml of a 1:1 chloroform-benzene solution and then with ether. An off-white solid, 132 mg (45%) with $\nu(\text{O-H})$ at 3550 cm^{-1} , was thus obtained. A pure white product was obtained by recrystallization from hot dichloromethane, mp 280–282° dec. Substitution of $\text{Pd}(\text{PPh}_3)_2\text{O}_2$ for $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ or of NOF_6 for NOBF_4 gave substantially the same results. Anal. Calcd for $\text{C}_{72}\text{H}_{62}\text{O}_2\text{P}_4\text{Pt}_2\text{B}_2\text{F}_8$: C, 52.5; H, 3.79. Found: C, 51.3; H, 3.62. Molar conductivity of 5×10^{-4} M nitromethane solution at 25°C, 169 $\text{ohm}^{-1}\text{cm}^2$.

Method B. A mixture of 2 drops of aqueous 48% HBF_4 in 5 ml of chloroform was added to 117 mg of $\text{Pt}(\text{PPh}_3)_2\text{O}_2$. The initially clear solution gradually became cloudy. After 1 hr the mixture was filtered and the residue, 85 mg (66%) of $[\text{Pt}_2(\text{PPh}_3)_4(\text{OH})_2][\text{BF}_4]_2$, was washed with ether.

Diacetonitrilebis(triphenylphosphine)platinum(II) Tetrafluoroborate ($[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$). A flask containing a solution of 72 mg of NOBF_4 in 5 ml of acetonitrile was attached to a vacuum line and the contents were degassed by the freeze-thaw method. The addition of powdered $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ (250 mg) from a side arm resulted in its dissolution and gas evolution was observed. After a few minutes the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and filtered. Addition of ether to the filtrate yielded 182 mg (56%) of fluffy white crystals, mp 237–239°C dec. Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{N}_2\text{P}_2\text{PtB}_2\text{F}_8$: C, 49.2; H, 3.72; N, 2.87. Found: C, 48.3; H, 3.72; N, 2.89. Molar conductivity of 5×10^{-4} M nitromethane solution at 25°C, 173 $\text{ohm}^{-1}\text{cm}^2$.

Tris(triphenylphosphine)platinum(II) Tetrafluoroborate ($[\text{Pt}(\text{PPh}_3)_3][\text{BF}_4]_2$). A mixture of 53 mg of $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$ and 47 mg of PPh_3 in 3 ml of dichloromethane was stirred for several hours under nitrogen. Upon addition of ether 57 mg (90%) of a finely divided white precipitate was obtained, mp 250–251°C dec. Anal. Calcd for $\text{C}_{54}\text{H}_{45}\text{P}_3\text{PtB}_2\text{F}_8$: C, 56.1; H, 3.92. Calcd for $\text{C}_{54}\text{H}_{47}\text{OP}_3\text{PtB}_2\text{F}_8$: C, 55.3; H, 4.04. Found: C, 55.5; H, 4.16. Molar conductivity of 5×10^{-4} M nitromethane solution at 25°C, 167 $\text{ohm}^{-1}\text{cm}^2$.

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Registry No. $[\text{Pt}(\text{PPh}_3)_2(\text{NO}_3)]_2[\text{BF}_4]$, 57016-55-4; $[\text{Pt}_2(\text{PPh}_3)_4(\text{OH})_2][\text{BF}_4]_2$, 34850-48-1; $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$,

57016-57-6; [Pt(PPh₃)₃][BF₄]₂, 57016-59-8; Pt(PPh₃)₂O₂, 29894-57-3; Pt(PPh₃)₂(C₂H₄), 12120-15-9; NOBF₄, 13826-86-3; HBF₄, 16872-11-0; PPh₃, 603-35-0.

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π -Allylmetal Chemistry. II.¹ A Novel Method to Prepare π -Allylplatinum(II) Complexes from Allylamines²

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The reactions of several allylic amines with cationic platinum(II) hydrides [PtH(PPh₃)₂L]ClO₄ (L = CO, AsPh₃, PPh₃) afford the complexes [Pt(π -allyl)(PPh₃)₂]ClO₄ and the amines in which the allylic group in the parent amines is replaced by hydrogen, in varying yields depending on the structure of the allylic moieties in the amines used: CH₂CH=CH₂ \approx CH₂CMe=CH₂ > CHMeCH=CH₂ > CH₂CH=CHMe-*trans*. The reactions of primary allylamines with PtH-(ClO₄)(PPh₃)₂ in benzene give *trans*-[PtH(PPh₃)₂(NH₂CHR¹CR²CHR³)]ClO₄ (R¹, R², R³ = H or Me) in which the existence of the Pt-N bonding is indicated by the infrared and ¹H NMR spectra. These amine adducts are converted slowly to the corresponding π -allyl complexes in methylene chloride at room temperature. Such a rearrangement is accelerated by the addition of a catalytic amount of CO, AsPh₃, or PPh₃. Different reactivity patterns of the formation of π -allylplatinum(II) complexes from allylamines and alcohols or ethers with cationic platinum(II) hydrides are discussed in terms of the differences in basicities of the nitrogen and oxygen donors toward both platinum and proton.

Introduction

Several allylic compounds have been employed to obtain π -allylmetal complexes depending on the type of metallic reagents used. Allyl halides are probably most frequently used in, e.g., oxidative addition to low-valent metallic compounds, nucleophilic substitution with complex metal anions, and the preparation of the Grignard reagents for metathesis.³ Allylic alcohols and esters can also be utilized to prepare π -allyl complexes of Ni(II) and Pd(II)⁴⁻⁶ where a high nucleophilicity of the metal atom in the low oxidation state as in Ni(CO)₄ or bis(1,5-cyclooctadiene)nickel may well be a driving force for the C-O bond cleavage by displacing the hydroxyl or carboxyl anions. In other reactions, a different route involving elimination of CO₂ or aldehydes was suggested to be a key step in the formation of π -allylplatinum(II) complexes from allyl alcohols or ethers and carbonyl-^{1,7} or hydridoplatinum(II)⁸ complexes. However, little is known of the use of allylic amines for formation of π -allyl complexes except in the preparation of 3-allylacetylacetones from allylamines and acetylacetone catalyzed by a palladium complex⁹ in which formation of an intermediate π -allyl complex may play an important role. The reason for the lesser utilization of the

allylamines as compared to halides or alcohols for the formation of π -allyl complexes is possibly related, in part, to the fact that the amino anions are much less effective leaving groups than the halide and hydroxyl anions. Here we report a facile conversion of various allylamines to π -allylplatinum(II) complexes induced by cationic platinum(II) hydrides with a concomitant substitution of the hydrogen atom for an allylic group in the parent amines, a reaction which appears to be potentially applicable to some organic syntheses.¹⁰

Experimental Section

Materials. Allylamine and diallylamine were purchased from Nakarai Chemicals Ltd. *trans*-Crotylamine, 2-methylprop-2-enylamine, and 1-methylprop-2-enylamine were prepared from the corresponding allylic chlorides by the Gabriel phthalimide method.¹² *N*-Allylethylamine¹³ and *N*-allyldiethylamine¹⁴ were prepared by the literature methods. *N*-Allylacetamide was prepared from allylamine and acetyl chloride. Silver perchlorate was dried over P₂O₅. [PtH(PPh₃)₂L]ClO₄, where L = CO (Ia), PPh₃ (Ic), or pyridine, and PtH(ClO₄)(PPh₃)₂ (III) were prepared according to the literature methods.¹⁵ The complex [PtH(PPh₃)₂(AsPh₃)]ClO₄ (Ib) used in the reactions with allylamines was produced *in situ* by reacting III with AsPh₃ in a 1:1 mol ratio in methylene chloride. The deuteride PtDCl(PPh₃)₂ was prepared from Pt(PPh₃)₄ and DCl in benzene, and