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Zerovalent Platinum Chemistry. VIII*. The Reactions of Nitric Oxide with Tris- and Tetrakis (triphenylphosphine) Platinum(0)

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The lemon-yellow complex obtained on reacting tris- or tetrakis (triphenylphosphine)platinum(0) with nitric oxide under anaerobic conditions is formulated as a monomeric hyponitrite derivative of platinum(II), $Pt(N_2O_2)(PPh_3)_2$*, on the basis of chemical and spectroscopic evidence. Attempts to prepare the previously reported «binuclear nitric oxide complexes of palladium and platinum» were unsuccessful.*

Introduction

In the course of our research on the reactivity of zerovalent platinum and palladium triphenylphosphine derivatives towards small molecules[1] we have investigated the reaction of nitric oxide with the complexes $(PtPPh_3)_n$ ($n = 3,4$). While this work was in progress Pneumaticakis[2] briefly reported similar reactions involving the complexes $M(PPh_3)_4$ (M = Pd, Pt) and formulated the products as binuclear, metal-metal bonded nitrosyl derivatives, $[M(NO)(PPh_3)_2]_2$, on the basis of their diamagnetism and the results of some oxidative titrations. Our experiments fail to substantiate these findings and lead instead to a different product which we formulate as a hyponitrite derivative of platinum(II).

Results and discussion

The passage of purified nitric oxide, free from traces of nitrogen dioxide, into a completely deoxygenated benzene solution of tris- or tetrakis(triphenylphosphine)platinum leads to the separation of a lemon-yellow, microcrystalline material. The mother liquor, after evaporation to dryness and washing of the residue with a small volume of dichloromethane, occasionally affords a very small quantity of a white product.

The lemon-yellow complex, which is monomeric in chloroform solution, analyses correctly as $Pt(NO)_2(PPh_3)_2$ and melts at 125-128° with some decomposition. In the solid state the complex is stable to air for several days but it undergoes more rapid decomposition when maintained in solution. The complex does not show any infrared bands in the region 1950-1500 cm^{-1}, attributable to the presence of monomeric terminal nitrosyl ligands,[3] but possesses instead significant, strong absorptions at 1285, 1240, and 1062 cm^{-1} and is clearly not identical with the product (m.p. 248° infrared absorption 1328 cm^{-1}) reported by Pneumaticakis.[2] The white material, recovered in small yield from the mother liquors, was identified as $Pt(NO_2)_2(PPh_3)_2$ by comparison with an authentic specimen.[4] The yield of this latter product increased in the presence of traces of oxygen in accord with occurrence of the well-known reaction:[5]

$$Pt(PPh_3)_3 \xrightarrow{O_2} Pt(O_2)(PPh_3)_2 \xrightarrow{NO} Pt(NO_2)_2(PPh_3)_2$$

Nitric oxide reacted with $Pd(PPh_3)_4$ in benzene solution or ether suspension under anaerobic conditions to yield a very unstable material which we were unable to isolate in a pure state; in the presence of traces of oxygen the same reagents afforded small amounts of $Pd(NO_2)_2(PPh_3)_2$, identical with an authentic specimen.[4] The reactions of nitric oxide with the zerovalent d^{10} nickel complexes, $Ni(CO)_4$ and $Ni(CO)_2(PPh_3)_2$, have previously been reported[6,7] to afford Ni^{II} dinitro derivatives; in one case formation of the hyponitrite complex, $[Ni(NO)(PPh_3)_2]_2N_2O_2$, has also been postulated.[6]

Repeated experiments, performed independently in London and Milan failed to yield the dinuclear complexes $[M(NO)(PPh_3)_2]_2$ reported by Pneumaticakis or furnish any evidence of their formation under the conditions employed.

We have therefore investigated the nature of the lemon-yellow platinum complex isolated from our reaction of nitric oxide with $Pt(PPh_3)_3$. The three strong, characteristic absorptions in the infrared spectrum of this product at 1285, 1240, and 1062 cm^{-1} all lie outside the range 1950-1500 cm^{-1}, usually associated with terminal nitrosyl ligands[3] but are consistent with the presence of a hyponitrite ligand. Thus the infrared spectrum of the dinuclear cation

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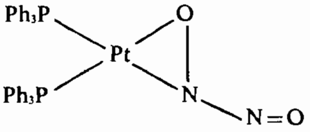
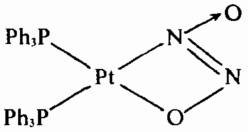
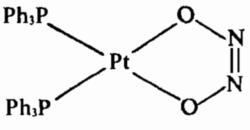
$\{[Co(NH_3)_5]_2N_2O_2\}^{4+}$ shows bands at 1136, 1046, and 932 cm^{-1} assigned,[8] on the basis of ^{15}N substitution data, to the vibrations of the asymmetrically bonded hyponitrite ligand. In sodium hyponitrite, where the $N_2O_2^{2-}$ anion has a *trans* configuration, the corresponding absorptions occur at 1383, 1115 (Raman) and 1020 cm^{-1} (infrared).[9] It follows that the probable presence of the hyponitrite ligand may be inferred from the infrared spectrum and this has been confirmed by chemical evidence. Treatment of the complex with dilute HCl yields $PtCl_2(PPh_3)_2$ and N_2O,[8] whilst the heterogeneous reaction between $PtCl_2(PPh_3)_2$ and sodium hyponitrite affords a product mixture which clearly shows infrared absorptions at 1285, 1240, and 1062 cm^{-1} in good agreement with those observed for the complex $Pt(NO)_2(PPh_3)_2$.

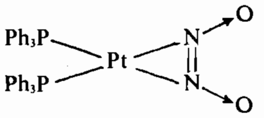
Coupling of two NO groups to form a bridging hyponitrite anion has previously been reported to occur at d^{10} Nickel(0) in the formation of $[Ni(NO)(PPh_3)_2]_2N_2O_2$[6] and similar reactions afford the hyponitrite bridged species $\{[MoCl(NO)(diarsine)]_2N_2O_2\}^{2+}$ (ref. 10) [diarsine = o–$C_6H_4(AsMe_2)_2$], $\{[Co(NH_3)_5]_2N_2O_2\}^{4+}$ (ref. 11) and $\{[Co(CN)_5]_2N_2O_2\}^{6-}$ (ref. 12). The ease with which zerovalent d^{10} complexes undergo two electron transfer probably contributes to the relatively facile manner in which formation of the platinum(II) hyponitrite complex occurs.

Firm conclusions concerning the structure of the hyponitrite complexes cannot be reached on the basis of the available infrared and chemical evidence alone; however some tentative ideas on this subject may be advanced. The complex being monomeric in solution ($CHCl_3$ or C_6H_6) the only probable structures are the following:

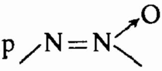

(I)


(II)


(III)


(IV)

The absence of a band attributable to ν(NO) for the nitrosamine (>N–N=O) group at *ca.* 1430-1500 cm^{-1} eliminates (I) as a probable structure.[13] Structure (II) involving an asymmetric *trans* conformation of the N_2O_2 group also appears improbable; in $\{[Co(NH_3)_5]_2N_2O_2\}^{4+}$, the only species in which a structure of this type has been rigorously established[14] for the $N_2O_2^{2-}$ ligand (albeit a bridging one), the infrared bands attributable to this ligand occur at appreciably lower frequencies (1136, 1046, and 932 cm^{-1})[8] than those recorded for the platinum hyponitrite complex. The two remaining symmetrical structures (III) and (IV) are less readli distinguished. A bridging $N_2O_2^{2-}$ ligand, coordinated through the two oxygen atoms, as in structure (III) has been postulated for the molybdenum complex $\{[MoCl(NO)(diarsine)]_2N_2O_2\}Cl_2$ and infrared bands at 1160, 1030 and 970 cm^{-1} have been assigned to the hyponitrite ligand.[10] However, the structure of this complex has yet to be confirmed. No examples of complexes containing the hyponitrite ligand coordinated through both nitrogen atoms as in structure (IV) have been reported to date.

However, related structures involving three membered ring systems are known for platinum complexes containing electrophilic ligands. These include $PtO_2(PPh_3)_2$[15] and $Pt(NCCF_3)(PPh_3)_2$.[16] Furthermore, the preference of platinum(II) for N– rather than O– coordination in complexes similar to the one under discussion is revealed by formation of the dinitro complex $Pt(NO_2)_2(PPh_3)_2$ rather than the dinitrito isomer. Finally the appearance of strong infrared bands at 1285 and 1240 cm–^{1}, typical[13] of ν(NO) for the azoxy group  $\diagup N{=}N\begin{smallmatrix}\nearrow O\\ \searrow\end{smallmatrix}$, is consistent with structure IV. On the basis of this evidence, the latter structures is marginally preferred. However, only an X-ray diffraction study can conclusively solve this problem.

Experimental

Zerovalent platinum triphenylphosphine complexes were prepared by literature methods.[17] Nitric oxide was generated from sodium nitrite and dilute sulphuric acid, and purified by washing with concentrated sulphuric acid followed by passage over potassium hydroxide pellets. All solvents were degassed and all reactions performed in a nitrogen atmosphere. Infrared spectra were taken on a Perkin-Elmer 457 spectrometer and molecular weights obtained using a Mechrolab osmometer. Analyses by Dr. Strauss, Oxford, and the analytical laboratory of Milan University.

Reaction of tris– or tetrakis (triphenylphosphine) platinum(O) with nitric oxide – $Pt(PPh_3)_3$ (2.4g) or $Pt(PPh_3)_4$ (3.0g) was dissolved in benzene under nitrogen, after complete dissolution a stream of purified nitric oxide was bubbled through the solution for 10 min. followed by a stream of nitrogen for a further 15 min. The resultant suspension was filtered and the *lemon-yellow* microcrystals washed successively with benzene and diethyl ether, then dried *in vacuo* to afford the required product 1.7g (mp. 125-128° with decomp.). Found C, 55.35; H, 4.15; N, 3.4; O, 3.75; P, 8.2% M.Wt. 770($CHCl_3$). $C_{36}H_{30}N_2O_2P_2Pt$ requi-

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res C, 55.5; H, 3.9; N, 3.6; O, 4.1; P, 7.95%; M.Wt. 779. Evaporation of the mother liquor from the above reaction afforded a yellow solid which, on washing with a small volume of dichloromethane left a less soluble component. This latter product was identified by its mp. (260°) and infrared spectrum [$\nu(NO_2)$1400, 1330 and 820 cm^{-1}] as $Pt(NO_2)_2(PPh_3)_2$.

Reaction of tetrakis(triphenylphosphine)palladium with nitric oxide. $Pd(PPh_3)_4$ (0.3g.) in degassed benzene gave a yellow solution which, on treatment with nitric oxide, turned green then pale yellow. After 0.5hr. the yellow solution was treated with degassed pentane and a yellow material precipitated. This product could not be purified. A similar reaction performed in the presence of traces of oxygen gave an impure solid which was identified as $Pd(NO_2)_2(PPh_3)_2$ by its infrared spectrum.

Reaction of cis-dichlorobis(triphenylphosphine) platinum with sodium hyponitrite. *cis*-$PtCl_2(PPh_3)_2$ (1.0g.) and $Na_2N_2O_2$ (1.5g.) were suspended in chloroform (40 ml). Slow reaction occurred after addition of ethanol (1 ml.) and afforded a pale yellow solution after 1.5hr. Evaporation to dryness under vacuum gave a yellow solid mixture which contained in its infrared spectrum the absorption bands typical of $Pt(N_2O_2)(PPh_3)_2$.

Reaction of $Pt(N_2O_2)(PPh_3)_2$ with hydrogen chloride. $Pt(N_2O_2)(PPh_3)_2$(0.5g.) suspended in ethanol under a nitrogen atmosphere was treated with dilute hydrochloric acid and the evolved gas collected in a gas burette; analysis by gas chromatography confirmed the presence of N_2O. The solid residue was characterized as *cis*-$PtCl_2(PPh_3)_2$ by comparison with an authentic specimen.

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