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Synthesis and Reactions of a New Pt(0) Complex with *o*-Nitrosoaniline

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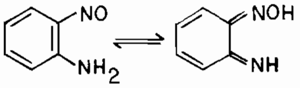
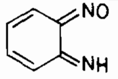
There has been great interest in the preparation and study of Pt(0) complexes due to their importance in catalysis and organic synthesis. *p*-Benzoquinone, coordinated to Pt(0), has been found to undergo some oxidative addition reactions and hydroquinone derivatives in addition to Pt(II) complexes have been isolated [1].

Recently some nitroso complexes of Pt(0) of the type $Pt(Ph_3P)_2(RNO)$ ($R = Ph, Bu, CF_3$) have been synthesized and their reactions have been investigated [2]. Studies on the reactions of nitroso compounds are of interest because they are probable intermediates in the reduction by carbon monoxide of nitro compounds, catalyzed by transition metal complexes [2].

We have previously investigated the reactions of some nitrosoamines with various transition metal ions [3, 4]. It has been reported that *o*-nitrosoaniline (**Ia**) tautomerizes in solution to give *o*-benzoquinone-imine-oxime (**Ib**) [5].



Ia **Ib**



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Moreover, in its complexes we found that *o*-nitrosoaniline behaved as a neutral (**Ib**, AH_2) or anionic (**II**, AH) ligand, coordinating to metals via the imine-oxime groups. We report here the isolation and some reactions of a new Pt(0) complex with *o*-nitrosoaniline.

Experimental

o-Nitrosoaniline was prepared by the method of Haddadin *et al.* [6]. Tetrakis-(triphenylphosphine)-platinum(0), $Pt(Ph_3P)_4$, was prepared by the method of Malatesta and Cariello [7].

The Synthesis of $Pt(Ph_3P)(AH_2)$

A solution of *o*-nitrosoaniline (0.5 mmol) in benzene (10 ml) was added to a stirred solution of $Pt(Ph_3P)_4$ (0.5 mmol) in benzene (10 ml). After 2 h of stirring, the solution was evaporated under reduced pressure and n-hexane was added to produce a deep violet precipitate. It was filtered off, washed with hot n-hexane and dried *in vacuo* over P_2O_5. *Anal.* Calc. for $Pt(Ph_3P)(AH_2)$: C, 49.74; H, 3.66; N, 4.83, Found: C, 49.13; H, 3.65; N, 4.73%. Melting point (m.p.) 152 °C.

The Reactions of $Pt(Ph_3P)(AH_2)$ with Organic Halides

The complex $Pt(Ph_3P)(AH_2)$ was reacted with CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and C_6H_5COCl using a similar procedure as illustrated for the reaction with CH_3I. A benzene solution of the complex (0.5 mmol), prepared without isolation, was treated with excess CH_3I (15 ml) at room temperature. After 24 h of stirring, the product formed was filtered off, washed with benzene and recrystallized from dichloromethane. The resulting pale yellow solid was identified as *cis*-$Pt(Ph_3P)_2(I)(CH_3)$. The filtrate was evaporated to dryness, digested with methanol and filtered. The residue was recrystallized from benzene to give *trans*-$Pt(Ph_3P)_2(I)(CH_3)$. The latter filtrate was chromatographed on a silica gel plate and eluted with a 5:1 mixture of benzene and petroleum ether (boiling point (b.p.) 40–60 °C). An orange–yellow complex $Pt(Ph_3P)_2I_2$ and an olive green solid which analyzes for $Pt(Ph_3P)(AH)(I)$ were isolated. *Anal.* Calc. for $Pt(Ph_3P)(AH)(I)$: C, 40.86; H, 2.86; N, 3.97. Found: C, 40.98; H, 3.03; N, 3.80%. m.p. 170 °C. The complexes $Pt(Ph_3P)_2I_2$ and *cis*- and *trans*-$Pt(Ph_3P)_2(I)(CH_3)$ were identified by elemental analyses and by comparison with authentic samples prepared by literature methods [7–9].

When the isolated complex $Pt(Ph_3P)(AH_2)$ was reacted with CH_3I in a similar manner as above, only $Pt(Ph_3P)(AH)(I)$ was formed.

The reaction of $Pt(Ph_3P)(AH_2)$ with C_2H_5I afforded the following compounds: $(Ph_3PC_2H_5)^+I^-$ (m.p. 165 °C), $Pt(Ph_3P)(AH)(I)$ and $Pt(Ph_3P)_2I_2$. However, the reactions of $Pt(Ph_3P)(AH_2)$ with $C_6H_5CH_2Cl$ and C_6H_5COCl gave $Pt(Ph_3P)_2Cl_2$ as a major product.

Infrared spectra were recorded on a Pye Unicam Model SP3-300 IR spectrophotometer using KBr pellets.

The NMR spectrum of *cis*-$Pt(Ph_3P)_2(I)(CH_3)$ in $CDCl_3$ was recorded on a Varian T-60A spectrometer using TMS as an internal standard.

Carbon, hydrogen and nitrogen analyses were carried out by Pascher Microanalytisches Laboratorium.

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Results and Discussion

The reaction of $Pt(Ph_3P)_4$ with *o*-nitrosoaniline in benzene at room temperature resulted in the formation of the Pt(0) complex $Pt(Ph_3P)(AH_2)$. The infrared spectrum of the latter complex is very similar to the spectra of other nitrosoamine complexes prepared in these laboratories [3, 4] and having the quinone-imine oxime moiety. The spectrum of $Pt(Ph_3P)(AH_2)$ shows bands at 3340 and 3040 cm^{-1} which are assigned to the ν(O–H) and ν(N–H) vibrations, respectively. The bands appearing at 1600 and 1500 cm^{-1} are ascribed to ν(C=N) vibrations while the bands at 1480 and 1000 cm^{-1} are assigned to the ν(P–Ph) vibrations.

The observed downward shifts (100–200 cm^{-1}, as compared to the other nitrosoamine complexes [3, 4]) in the O–H and N–H stretching frequencies indicate the presence of strong back-donation from Pt(0) to the ligand. Thus, the neutral ligand AH_2 is proposed to coordinate to Pt(0) through the two ortho nitrogens of the imine and oxime groups.

Similarly, 1-nitroso-2-naphthylamine and 2-nitroso-1-naphthylamine have been found to tautomerize to the corresponding quinone-oxime and to coordinate to metals via the nitrogen atoms [10–12].

The reaction of the isolated complex $Pt(Ph_3P)(AH_2)$ with CH_3I at room temperature gave a Pt(II) complex formulated as $Pt(Ph_3P)(AH)(I)$. This reaction may proceed by the oxidative addition of CH_3I to the tri-coordinate Pt(0) complex $Pt(Ph_3P)(AH_2)$ to give an unstable five-coordinate intermediate $Pt(AH_2)(Ph_3P)(CH_3)(I)$ which decomposes to give $Pt(Ph_3P)(AH)(I)$ and probably methane. However, methane could not be detected easily under these conditions. It is worth mentioning here that attempts to prepare Pt(II) complexes with *o*-nitrosoaniline, starting with Pt(II) salts, were unsuccessful.

The infrared spectrum of the complex $Pt(Ph_3P)(AH)(I)$ is characterized by the presence of a band at 3400 cm^{-1} which is assigned to the ν(N–H) vibrations, while there is no other band in this region which can be contributed to the presence of a ν(O–H) vibration. The rest of the spectrum is similar to that of $Pt(Ph_3P)(AH_2)$ thus indicating the presence of the anionic ligand AH in the quinone-imine oxime form (**II**). The bands appearing at 1570 and 1535 cm^{-1} are assigned to the ν(C=N) vibrations, those at 1485 and 1032 cm^{-1} to the ν(Ph–P) vibrations.

However, when the complex $Pt(Ph_3P)(AH_2)$ was prepared in solution and then reacted directly with CH_3I, the following complexes were isolated: $Pt(Ph_3P)(AH)(I)$, *cis*- and *trans*-$Pt(Ph_3P)_2(I)(CH_3)$ and $Pt(Ph_3P)_2I_2$. The *cis*-$Pt(Ph_3P)_2(I)(CH_3)$ complex has been recently reported by Zaghal and Tayim [8] from the reaction of CH_3I with $Pt(QI)(Ph_3P)_2$ (QI = *p*-$PhOCN{=}C_6H_4{=}NCOPh$).

The NMR spectrum of *cis*-$Pt(Ph_3P)_2(CH_3)(I)$ exhibits a doublet at δ3.1 and 3.2 ppm that is assigned to the methyl groups and a doublet at 7.63 and 7.77 ppm which is assigned to the phenyl groups of triphenylphosphine.

The *cis*-$Pt(Ph_3P)_2(I)(CH_3)$ complex is expected to be kinetically less stable than the *trans* isomer with respect to methyl substitution due to the strong *trans*-effect of the triphenylphosphine group. Therefore, it may easily undergo a rapid substitution reaction in the presence of excess CH_3I to give *cis*-$Pt(Ph_3P)_2I_2$.

It is known that Pt(0) complexes may undergo dissociation in solution. Hence, the Pt(0) complex $Pt(Ph_3P)(AH_2)$ could be formed from the dissociation of $Pt(AH_2)(Ph_3P)_2$ as shown below

$$\underset{\text{4-coordinate}}{Pt(Ph_3P)_2(AH_2)} \rightleftharpoons \underset{\text{3-coordinate}}{Pt(Ph_3P)(AH_2)} + Ph_3P$$

The *cis*-$Pt(Ph_3P)_2(I)(CH_3)$ complex is likely to be formed by the oxidative addition of CH_3I to $Pt(Ph_3P)_2(AH_2)$ followed by decomposition of the addition intermediate.

Moreover, the reaction of C_2H_5I with $Pt(Ph_3P)(AH_2)$, prepared in solution, gave $Pt(Ph_3P)(AH)(I)$ and $(Ph_3PC_2H_5)^+I^-$ while the reaction with benzyl and benzoyl chloride gave $Pt(Ph_3P)_2Cl_2$ as a major product.

The complex $Pt(Ph_3P)(AH_2)$ thus contains the quinone-imine oxime form (**Ib**) of *o*-nitrosoaniline (**Ia**) and its reactions with organic halides gave Pt(II) derivatives only. However, these reactions still have to be investigated to test for organic addition products.

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