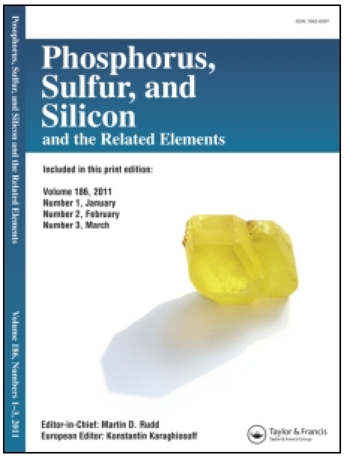

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Synthesis and Characterization of a Novel Phosph(V)azane-Platinum(II) Complex

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Synthesis and Characterization of a Novel Phosph(V)azane-Platinum(II) Complex

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The substitution reaction of bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$ **(1)** *with trans-*$PtCl_2(SEt_2)_2$ *yields the novel unprecedented phosph(V)azane-platinum complex cis-*$Pt(SEt_2)_2Cl[HNPhP(O)NPh(HNEt_3)]$ **(3)**. *In this reaction, the bis(anilino)phosphine oxide undergoes P–H activation and a Pt(II)–P(V) bond instead of Pt–N bond forms.* ^{31}P *NMR spectra readily distinguish between the "N" and "P" bonding modes. The reaction requires the presence of triethylamine (TEA) as a base in order to deprotonate the phosphazane ligand and is separated as* $Et_3NH^+Cl^-$*, whereas* $HTEA^+$ *exists in the final product* ***3*** *and is acting as charge balancing and H-bond structure directing agent. The products have been fully characterized by means of IR; MS; UV-Vis; and* ^1H, ^{13}C, *and* ^{31}P *NMR spectroscopy.*

Keywords Bis(anilino)phosphine oxide; charge balancing; P-H activation; phosphazane ligand; platinum complex

INTRODUCTION

Over the past decade, there has been a growing interest in the synthesis of anionic phosph(V)azanes as anions of the p-block elements and as their alkali-metal derivatives in view of their possible applications in catalysis and their ability to stabilize unusual geometries at metal centers.[1–3] In these anionic forms of the phosph(V)azans, there are different coordination modes involving the "hard" (N, O) and the "soft" (S, Se, Te) centers for generation of chelation complexes containing various metals with main group and transition metals.[4–9] The anionic forms can be produced using organolithium reagents such as n-butyllithium (Bu^nLi) as a deprotonating base in which anions bind to Li^+ via nitrogen

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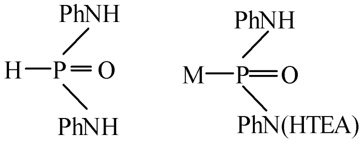
or chalcogen atoms such as in the syntheses of a Pt(II) (S,S′) complex $Pt(PEt_3)_2[(^tBuN)(S)P(\mu\text{-}N^tBu)_2P(S)(N^tBu)]$ by Chivers et al.[10]

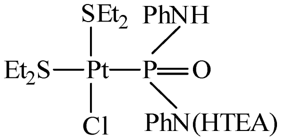
Our studies, including the investigation of the synthesis and coordination chemistry of some acyclic phosph(V)azans, led us to study the novel ligand bis(anilino)phosphine oxide, $(C_6H_5NH)_2P(O)H$ **(1)**, which contains both “hard” N and O coordination sites (Scheme 1).[11,12]



1 **2**

SCHEME 1

In the present work, triethylamine is used as the deprotonating base instead of Bu^nLi, and the ligand is converted to an unprecedented feature of type **2** in which the cation $HNEt_3^+$ exists as counter ion and in a hydrogen bond in the anion. It is notable that in the phosph(V)azane complexes with chalcogenido substituents, the ligand is usually coordinated through nitrogen or chalcogen. To the best of our knowledge, the coordination through phosphorus has been explored only in phosph(III)azanes such as the molybdenum phosph(III)azane complexes.[13–16] But interestingly, herein the ligand has been attached to platinum through a phosphorus atom in the novel compound **3**; we describe these observations in this article (Scheme 2).



3

SCHEME 2

RESULTS AND DISCUSSION

In the present work, bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$ **(1)** is reproduced according to an improved procedure with a better yield than that previously reported one[11] as indicated in Equation (1):

$$PCl_3 + 2PhNH_2 + H_2O \xrightarrow{80^\circ C} (C_6H_5NH)_2P(O)H + 3HCl \qquad (1)$$

In this reaction, the interaction of PCl_3 with $PhNH_2$ in a molar ratio of 1:5 results in the stepwise replacement of PhNH and finally formation of $(PhNH)_3P$, which is converted to $(PhNH)_2P(O)H$ upon addition of H_2O in a controlled hydrolysis reaction with the elimination of aniline (yield 84%).[12] Then the ligand $(C_6H_5NH)_2P(O)H$ **(1)** was reacted with trans-$PtCl_2(SEt_2)_2$ in the presence of an excess of triethylamine (TEA) to synthesize a novel complex **3** containing a Pt(II)–P(V) bond. P–H activation occurs in the presence of TEA as the base and interestingly, herein the ligand is finally attached to platinum(II) by phosphorus(V). *Trans*-$PtCl_2(SEt_2)_2$ was prepared according to the literature method.[17] Stirring a solution of **1** and *trans*-$PtCl_2(SEt_2)_2$ without NEt_3 resulted in no net reaction, and the starting materials were quantitatively recovered from the reaction mixture. This observation could be interpreted based on the hard and soft acid-base principle, which states that a hard acid prefers to react with a hard base and a soft acid prefers to react with a soft base.[18] In this complex, the phosphorus atom, which behaves as a soft donor, is coordinated to platinum(II) as a soft Lewis acid.[19] Therefore, there are stronger interactions between them rather than interaction with nitrogen or oxygen as hard atoms.

The addition of *trans*-$PtCl_2(SEt_2)_2$ to $(C_6H_5NH)_2P(O)H$ in the ratio of 1:1 in the presence of an excess of TEA affords the unprecedented complex *cis*-$Pt(SEt_2)_2Cl[HNPhP(O)NPh(HNEt_3)]$ **(3)** as deep red powder in 80% yield (Equation 2).

$$\begin{gathered}(C_6H_5NH)_2\,P(O)H + \textit{trans}\text{-}PtCl_2\,(SEt_2)_2 \xrightarrow[\text{THF, }25^{\circ}\text{C}]{NEt_3} \\ cis\text{-}Pt(SEt_2)_2Cl[HNPhP(O)NPH(HNEt_3)] + EtNH^{+}Cl^{-} \\ \mathbf{3}\end{gathered} \tag{2}$$

Multinuclear (^{31}P, ^{1}H, and ^{13}C) NMR spectra indicate that $(C_6H_5NH)_2P(O)H$ **(1)** is bonded to Pt(II) through the phosphorus atom. The ^{31}P NMR spectrum in $CDCl_3$ exhibits one doublet with $^{2}J_{PNH} =$ 10.50 Hz and with ^{195}Pt satellites and no coupling with a directly bonded hydrogen. Also the $^{31}P\{^{1}H\}$ NMR spectrum shows only a singlet that is flanked with ^{195}Pt satellites. The ^{1}H NMR spectrum of **3** consists of two equally intense resonances at δ 1.39 and 1.43, corresponding to CH_3 protons in one pair of SEt_2 and 2.71 and 3.25 ppm for CH_2 protons as broad multiplets in SEt_2 according to a *cis* geometry for SEt_2 groups with the appropriate relative intensities. The methylene protons are coupled to the CH_3 protons as well as to platinum. However, no coupling constants were measurable. There was no indication of the presence of a P–H bond in **3** from either the ^{1}H NMR or IR spectra.

The one NH group that remained intact was observed at δ 7.52 as a doublet with $^2J_{\mathrm{NHP}} = 8.58$ Hz, and the presence of HTEA$^+$ protons at 1.30, 3.04, and 11.07 ppm suggests that the second NH group appeared as the protonated HTEA$^+$ cation in the product. Triethylamine was applied to deprotonate the ligand, but based on the IR and ^{1}H NMR evidence, HTEA$^+$ exists in the final product **3**. It may be assumed that the HTEA$^+$ cation has a charge-balancing role and is acting as an H-bond structure-directing agent. A similar situation is reported in the synthesis of conventional zeolites such as phosphates and triethylammonium benzene-1, 3,5-tricarboxylato (pyridine) zinc (II).[20–22]

The ^{13}C{^{1}H} NMR spectrum of **3** contains aliphatic and aromatic carbons with six and eight signals, respectively, which agree well with the proposed structure **3** and are consistent with a C_1 symmetry. On the other hand, IR results exhibit characteristic bands. The NH stretching bonds are observed at 3407 and 3212 cm^{-1} in **3**, which are assigned to HTEA$^+$ and HNP, respectively. The amido NH vibration shifted by 20 cm^{-1} to a higher frequency, while the P=O stretching showed no variation, indicating that this bond has remained intact.

The mass spectrum of **3** was recorded with a FAB positive source. The mass data are easily related to the proposed structure, with the normal loss of $\mathrm{HNEt_3^+}$, and fragments arising from the entity and the ligand. The molecular ion peak is observed at m/z 742 with a quasi-ion peak at m/z 727, which could be attributed to loss of a CH_3 group from the complex. Other peaks are also observed at m/z values of 526 [Pt(NHPh)P(O)NPh(HTEA)], 427 [Pt(NHPh)P(O)NPh], 410 [$(\mathrm{SEt_2})_2$PtCl], 375 [$(\mathrm{SEt_2})_2$Pt], 323 [P(O)NPh(HTEA)], 295, 275, 255, 230, 213, 195, 196, 122 (PNPh), 102 (HTEA), 93 ($\mathrm{PhNH_2}$), 86 ($\mathrm{H_2CNEt_2}$), 78, 77, 75, 66, 65, 61, 47, which could easily be assigned in terms of the envelopes.

The electronic absorption bands for the complex **3** measured in THF solution in the range of 200–800 nm are at 239, 510, and 546 nm. The broad band at 239 nm is assigned to the π–π^* transitions of the phosphazane ligand. The color of this complex (deep red) is attributed to an MLCT band.[23–29] The electronic spectra are characterized by two absorbances, which we suggest to be an MLCT (d_π–π^*) transition, and the π^* belongs to the P=O bond. The energies of these bands were sensitive to the nature of the solvent. In the presence of light, a hypsochromic shift (blue shift) is observed in THF, and an increase in the intensity of absorption in the band with higher energy (shoulder, 510 nm) and a decrease in the intensity of absorption in the band with lower energy (546 nm) was observed, but in $CHCl_3$ there were no shifts in the bands. More research is currently in progress to develop these types of photochemistry.

It is notable that the quantitative determination of chloride in the product and in the by-products showed the existence of one equivalent chloride in **3**. In addition, the compound had just one spot on TLC, which indicates the existence of only one type of product. All attempts to grow single crystals of this new complex suitable for X-ray crystallography were unsuccessful.

CONCLUSION

The reaction of one equivalent of **1** with Pt(II) complex in the presence of TEA results in the elimination of HCl and formation of $Et_3NH^+Cl^-$ to generate the novel compound *cis*-$Pt(SEt_2)_2Cl[HNPhP(O)NPh(HNEt_3)]$ **(3)**. The spectroscopic data indicate **2** coordinates in a “P” fashion to the Pt(II) moiety, which is supported by hard and soft acid-base principles and $HTEA^+$, which resides in the interlayer space and plays an important role as a structural directing agent.

EXPERIMENTAL

Materials and Instrumentation

All manipulations were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran was treated with KOH and was freshly distilled twice from sodium before use. Diethyl ether, hexane, benzene, and toluene were treated with calcium chloride and distilled over sodium after refluxing for 5 h. Chloroform was distilled from P_4O_{10}. Aniline was distilled from CaH_2 and stored over molecular sieves. NEt_3 was dried over $MgSO_4$. Phosphorus trichloride and absolute ethanol were used as received from Merck Co.

The NMR spectra were recorded on a Bruker Avance 500 MHz at ambient temperature. ^1H (500.13 MHz) and ^{13}C NMR (125.77 MHz) were recorded using $CDCl_3$ as a solvent with TMS as an external standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR. The ^{31}P spectra (202.45 MHz) were referenced to external 85% H_3PO_4.

The IR spectra were measured on a Bomem FT-IR spectrophotometer, and the electronic absorption spectra were obtained on a JASCO 7850 UV-visible spectrophotometer.

The FAB(+) mass spectra were recorded using a JEOL SX-102A instrument.

Synthesis of *cis*-Pt(SEt_2)$_2$Cl [HNPhP(O)NPh($HNEt_3$)] (3)

trans-$PtCl_2(SEt_2)_2$ (0.192 g, 0.431 mmol) was dissolved in dry THF (10 mL) and added dropwise to a mixture of $(C_6H_5NH)_2$ P(O)H **(3)** (0.1g, 0.431 mmol) and NEt_3 (1 mL, excess) in dry THF (50 mL) under N_2 at 25°C in the absence of light. Then the mixture was stirred for 3 days. $NEt_3H^+Cl^-$ was filtered off. The solvent was removed, and a deep red oily residue was obtained that was washed with diethyl ether. Then the red residue was redissolved in $CHCl_3$ and filtered. Diethyl ether was added dropwise at 0°C to the red filtrate to precipitate a red powder solid (yield 80%), mp 115°C dec.

IR (KBr): 3407 (br, $HNEt_3$), 3212 (m, HNP), 3048 (Ph), 2975–2873 (s, Et), 1451 (s, SEt_2), 1257 (s, SEt_2), 1193 (br, P=O), 1049, 760–692 (s, Ph) cm^{-1}.

^1H NMR (25°C, $CDCl_3$, ppm): 1.30 (t, $^3J_{HH} = 7.17$ Hz, 9H, $HNEt_3$), 1.39 (t, $^3J_{HH} = 7.45$ Hz, 6H, SEt_2), 1.43 (t, $^3J_{HH} = 6.87$ Hz, 6H, SEt_2), 2.71 (m, $^3J_{HH} = 7.03$ Hz, 4H, SEt_2), 3.04 (quartet, $^3J_{HH} = 6.78$ Hz, 6H, $HNEt_3$), 3.25 (m, $^3J_{HH} = 7.53$ Hz, 4H, SEt_2), 6.73–7.42 (m, 10H, Ph), 7.52 (d, $^2J_{PNH} = 8.58$ Hz, 1H, NH), 11.07 (s, br, 1H, $HNEt_3$).

$^{31}P\{^1H\}$ NMR (25°C, $CDCl_3$, ppm): −1.88 (s, $^1J_{PPt} = 2194$ Hz). ^{31}P NMR: −1.82 (d, $^2J_{PNH} = 10.50$ Hz, $^1J_{PPt} = 2180$ Hz).

$^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$, ppm): 7.46 (CH_3, SEt_2), 8.62 (CH_3, SEt_2), 12.46 (CH_2, SEt_2), 12.72 (CH_2, SEt_2), 31.83 (CH_3, $HNEt_3$), 45.93 (CH_2, $HNEt_3$), 117.23 (C_p, NPh), 119.96 (C_m, NPh), 121.62 (C_o, NPh), 122.62 (C_i, NPh), 128.88 (C_p, HNPh), 129.14 (C_m, HNPh), 129.31 (C_o, HNPh), 141.96 (C_i, HNPh).

UV-vis (THF, r.t.), λ_{max}[nm]: 546, 510, 239.

MS: *m/z* 727, 560, 526, 426, 410, 375, 323, 295, 275, 255, 230, 213, 195, 196, 122, 102, 93, 86, 78, 77, 75, 66, 65, 61, 47.

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