NEW COMPOUNDS

Five-Coordinated BF_3 Adducts of Platinum(II) Complexes

Hamadallah A. Hodali

Chemistry Department, Faculty of Science, University of Jordan, Amman, Jordan

The four-coordinated platinum(II) complexes [Pt(S-P)Cl_2], [Pt(S-As)Cl_2], and [Pt(S-P)I_2] were prepared, and their reactions with gaseous BF_3 and $(C_2H_5)_2O{\cdot}BF_3$ were studied. The isolated products, [Pt(S-P)Cl_2]·BF_3, [Pt(S-As)Cl_2]·BF_3, and [Pt(S-P)I_2]·BF_3, were characterized by tensimetric titrations with BF_3, IR and NMR spectra, conductivity measurements, and elemental analysis.

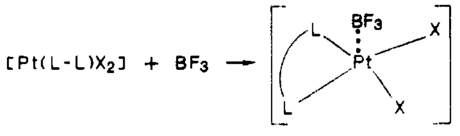
Introduction

Donor–acceptor interactions between planar d^8 complexes and molecular Lewis acids, such as BF_3, led to the preparation of several BF_3 adducts (*1–3*). However, reactions of platinum(II) compounds of the type [PtL_2X_2] (L = PPh_3, X = Cl, Br, I) with BF_3 led to the formation of cationic halogen-bridged species, $[PtL_2X]_2^{2+}{\cdot}2BF_3X^-$ (*4*, *5*).

Herein the effect of mixed donor bidentate ligands on the Lewis basicity of platinum(II) complexes, as reflected on their reactions with BF_3, is studied. The chelating ligands chosen for this study are 1-thiomethyl-2-diphenylphosphinoethane (S-P) and 1-thiomethyl-2-diphenylarsinomethane (S-As), which produce chelates that are stronger reductants or bases than the corresponding complexes with monodentate ligands.

Results and Discussion

The new complexes [Pt(S-P)Cl_2], [Pt(S-As)Cl_2], and [Pt(S-P)I_2], prepared in this study, show similar behavior in their tensimetric titrations with BF_3 and in their reactions with an etheral solution of BF_3. The break in the pressure–composition curve (Figure 1) indicates that 1 mol of BF_3 is consumed per mol of the platinum complex. Elemental analyses of the isolated platinum compounds and their BF_3 adducts are in good agreement with the formation of (1:1) acid–base adducts, eq 1.



(1)

L-L = S-P; X = Cl, I
L-L = S-As; X = Cl

IR of the BF_3 adducts show absorptions (1100–1050 cm^{-1}) due to coordinated BF_3 (*6*, *7*). NMR data of the ligands, the parent compounds, and their BF_3 adducts exclude possible interactions between the coordinated ligand and BF_3. The equivalent conductivities indicate that the platinum complexes and their BF_3 adducts are nonelectrolytes in nitromethane (*8*) (Table I).

Experimental Section

All chemicals used were of AR or GR grade and were dried as required. IR spectra were run on a Perkin-Elmer Model 577 spectrometer. Proton NMR spectra were obtained on a Varian T-60A spectrometer. Microanalyses were carried out by E. Pascher Microanalytical Laboratory (Bonn, W. Germany). Conductivity measurements were made with 10^{-3} M nitromethane solutions using digital conductivity meter Model PW 9527.

Table I. Infrared, Proton NMR, and Equivalent Conductivity Data

compound	γ(B–F), cm^{-1}	δ(S–CH_3), ppm	equiv conductance,[a] mho·cm^3·$equiv^{-1}$
S-P		2.07	
S-As		2.05	
[Pt(S-P)Cl_2]		2.70	23.5
[Pt(S-As)Cl_2]		2.70	12.2
[Pt(S-P)I_2]		2.73	3.0
[Pt(S-P)Cl_2]·BF_3	1062	2.70	31.3
[Pt(S-As)Cl_2]·BF_3	1062	2.77	26.0
[Pt(S-P)I_2]·BF_3	1060	2.73	25.4

[a] Conductivities measured in 10^{-3} M nitromethane solutions at 25 °C.

The ligands 1-thiomethyl-2-diphenylphosphinoethane (S-P) and 1-thiomethyl-2-diphenylarsinoethane (S-As) were prepared by the reaction of $Na^+P^-(C_6H_5)_2$ or $Na^+As(C_6H_5)_2$ with 2-chloroethyl methyl sulfide, respectively (*9*).

Preparation of the Complexes. (a) Dichloro(1-thiomethyl-2-diphenylphosphinoethane)platinum(II) [Pt(S-P)Cl_2] and dichloro(1-thiomethyl-2-diphenylarsinoethane)platinum(II) [Pt(S-As)Cl_2]: To a filtered solution of K_2PtCl_4 (0.21 g, 0.5 mmol) in water (10 mL) was added, with continuous stirring, a filtered solution of the ligand (0.5 mmol) in ethanol (10 mL). During the addition, an off-white solid started to precipitate. Stirring was then continued for 1 h. The solid precipitate was filtered, washed with a (1:1) acetone–water mixture, and then with diethyl ether, and finally dried under vacuum at 50 °C.

(b) Diiodo(1-thiomethyl-2-diphenylphosphinoethane)platinum(II) [Pt(S-P)I_2]: To a suspension of [Pt(S-P)Cl_2] (1.05 g, 2 mmol) in 50 mL acetone was added a filtered solution of KI (0.83 g, 5 mmol) in water (10 mL). The mixture was stirred at 50 °C for 12 h. The off-white solid slowly dissolved leading to the formation of a yellow precipitate. Solvent was removed under reduced pressure and the yellow residue was dissolved in CH_2Cl_2. The solution was filtered and diethyl ether was added to the filtrate. A yellow solid separated which was then filtered and dried under vacuum at 50 °C.

Tensimetric Titrations. The titration was done in a preparative high vacuum line (*10*). One millimole of the platinum complex [Pt(ligand)X_2] and a stirring bar were introduced into a round-bottomed flask which was then attached to the vacuum line. Dry CH_2Cl_2 (10 mL) was distilled into the flask and the mixture cooled to 0 °C. The vapor pressure of the solution was recorded. Successive amounts of BF_3 (~0.2 mmol) were distilled into the solution and the vapor pressure was recorded after each addition.

Preparation of the Adducts [Pt(S-P)Cl_2·BF_3 and [Pt(S-As)Cl_2]·BF_3. A suspension of [Pt(S-P)Cl_2] or [Pt(S-As)Cl_2] was prepared from 0.5 mmol of the complex in dry chloroform (30 mL). To this suspension was added dropwise and with continuous stirring $(C_2H_5)_2O{\cdot}BF_3$ (5 mmol BF_3). The suspended off-

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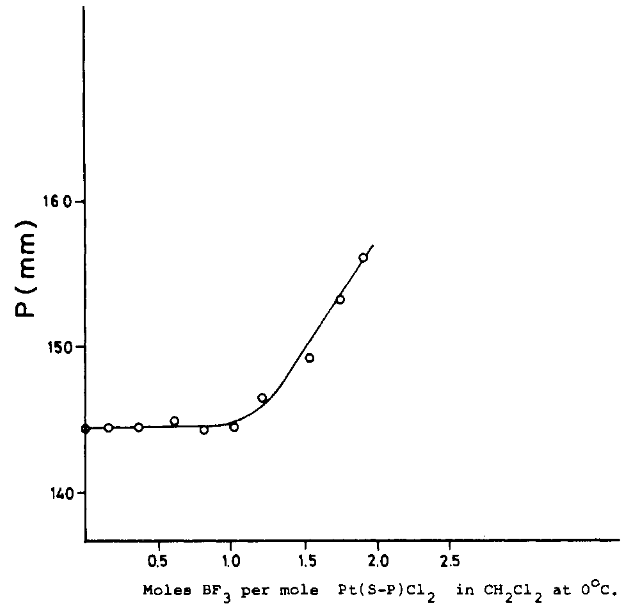

Figure 1. Tensimetric titration of Pt(S-P)Cl$_2$ with BF$_3$ at 0 °C.

white solid dissolved during the first few minutes of stirring forming a clear yellow solution. Stirring was continued at room temperature for 2 h. The solution was then filtered, and solvent was removed under reduced pressure. The pale-yellow residue was collected, washed with cold methanol (3 × 5 mL) and diethyl ether (20 × 10 mL), and then dried under vacuum at 50 °C.

Preparation of **[*Pt(S-P)I*$_2$]·*BF*$_3$.** To a stirred suspension of [Pt(S-P)I$_2$] (0.35 g, 0.5 mmol) in dry chloroform (30 mL) was added $(C_2H_5)_2O\cdot BF_3$ (5 mmol BF$_3$). The mixture was further stirred at room temperature for 2 h. The suspended yellow solid did not dissolve completely upon the addition of $(C_2H_5)_2O\cdot BF_3$ and a color change from bright yellow to orange-yellow was observed. The reaction mixture was filtered, the solid residue was discarded, and the filtrate was concentrated, under reduced pressure, to a volume of 10 mL. Addition of diethyl ether (30 mL) precipitated a pale-yellow solid which was then filtered, washed with diethyl ether, and dried under vacuum at 50 °C.

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Registry No. [Pt(S-P)Cl$_2$], 92763-60-5; [Pt(S-As)Cl$_2$], 108150-97-6; [Pt(S-P)I$_2$], 108150-98-7; [Pt(S-P)Cl$_2$]·BF$_3$, 108150-99-8; [Pt(S-As)Cl$_2$]·BF$_3$, 108151-00-4; [Pt(S-P)I$_2$]·BF$_3$, 108151-01-5; K$_2$PtCl$_4$, 10025-99-7; $(C_2H_5)2O\cdot BF_3$, 109-63-7.

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1,3-Dipolar Cycloaddition of Nitrile Oxides with *cis*- and *trans*-Ethylene-Substituted Δ^2-Isoxazoline Derivatives

Sultan T. Abu-Orabi* and Nawash M. Al-Ghezawi
Chemistry Department, Yarmouk University, Irbid, Jordan

1,3-Dipolar cycloaddition reactions of 2,4,6-trimethylbenzonitrile oxide with dimethyl maleate, dimethyl fumarate, and diethyl fumarate were used for the synthesis of polyfunctional 2-isoxazoline ring systems.

Nitrile oxides have been considered as one of the most important precursors for the synthesis of isoxazole and 2-isoxazoline ring systems upon their reaction with substituted acetylenes (*1–3*) and ethylenes (*4–7*), respectively. Continuing our previous work on the synthesis of polyfunctional heterocycles containing isoxazole and 2-isoxazoline ring systems (*8*), we report in the present paper further details on the reaction of 2,4,6-trimethylbenzonitrile oxide (I) with disubstituted ethylenes as shown in Scheme I.

Experimental Section

2,4,6-Trimethylbenzonitrile oxide was prepared as previously reported (*9*). Melting points were measured with a Buchi 510 capillary melting point apparatus. The nuclear magnetic resonance spectra were recorded on a Bruker AM 300 (300 MHz) using tetramethylsilane as an internal reference and shifts (δ) are reported in ppm. Elemental analyses were performed by the analytical Laboratory of the Universität Bielefeld, West Germany.

Preparation of cis-Dimethyl-3-(2,4,6-trimethylphenyl)-4,5-dihydro-4,5-isoxazoledicarboxylate (II). To a solution of 4.83 g (30 mmol) of freshly prepared 2,4,6-trimethylbenzonitrile oxide in 40 mL of tetrahydrofuran was added 4.61 g (32 mmol) of dimethyl maleate. The resulting mixture was heated under reflux for 6 h. Tetrahydrofuran was removed on a rotary evaporator at diminished pressure. Distillation of the yellow thick liquid yielded 7.5 g (82%) of the product, bp 150–155 °C/0.01 mmHg. The product was solidified near room temperature: mp 124–125.5 °C; NMR (CDCl$_3$) δ 6.86 (2 H, s), 5.56 (1 H, d, J = 6.4 Hz), 4.69 (1 H, d, J = 6.4 Hz), 3.84 (3 H, s), 3.59 (3 H, s), 2.26 (3 H, s), 2.17 (6 H, s).

trans-Dimethyl-3-(2,4,6-trimethylphenyl)-4,5-dihydro-4,5-isoxazoledicarboxylate (III). To a solution of 8.05 g (50 mmol) of freshly prepared 2,4,6-trimethylbenzonitrile oxide in 80 mL of tetrahydrofuran was added 7.63 g (53 mmol) of dimethyl fumarate. The resulting mixture was heated under reflux for 5 h. After removal of tetrahydrofuran on a rotary evaporator at diminished pressure, the residue was recrystallized from

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