

Unprecedented formation of isoxazole in the reaction between nitromethane and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in the presence of ethylene

Julian A. Davies,^a Constanze Petersohn^a and Vadim Yu. Kukushkin^{*b}

^a Department of Chemistry, College of Arts and Sciences, University of Toledo, Toledo, Ohio 43606-3390, USA

^b Department of Chemistry, St. Petersburg State University, 198904 Stary Petergof, Russian Federation

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The reaction in air between nitromethane and $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of ethylene gives isoxazole which has been trapped by platinum(II) through reaction with $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{PtCl}_4]$ to produce the isoxazole complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ which has been characterized spectroscopically, crystallographically and by independent synthesis.

Boron trihalides have proved to be useful reagents for the synthesis of bridged or solvato-complexes of platinum(II) through halide or pseudohalide abstraction reactions.¹ Previously, it has been reported that chloride abstraction from the platinum(II) complex $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{PtCl}_4]$ by $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 or MeCN produces the chloride-bridged dimer $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ ² or the acetonitrile solvato-complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{MeCN})]$,³ respectively. We here report that the reaction of $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{PtCl}_4]$ and “aged” $\text{BF}_3 \cdot \text{OEt}_2$, which was shown to contain dissolved ethylene, proceeds in a different way in nitromethane and results in the unprecedented formation of isoxazole, followed by the trapping of isoxazole by platinum(II).

Interaction of $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{PtCl}_4]$ and freshly distilled $\text{BF}_3 \cdot \text{OEt}_2$ in MeNO_2 at room temperature in air gave, exclusively, an as-yet-unidentified product, A.† If “aged” boron trifluoride-diethyl ether was used instead, a mixture of products was isolated—both the complex A and the isoxazole complex, $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$. The latter was separated from A and obtained in 10–15% yields after column chromatography on SiO_2 and characterized by X-ray diffraction (polymorph I; Fig. 1; see below).‡§ The reaction was found to be reproducible with “aged” samples of $\text{BF}_3 \cdot \text{OEt}_2$ purchased from Aldrich, Janssen and Wako. Monitoring of all these “aged” samples of $\text{BF}_3 \cdot \text{OEt}_2$ by ¹H NMR spectroscopy indicated the presence of $\text{CH}_2=\text{CH}_2$ (5.40 ppm in CDCl_3 vs. TMS) as the only additional component detectable by this method; ethylene presumably arises from decomposition of diethyl ether. When halide abstraction from $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{PtCl}_4]$ in nitromethane by freshly distilled $\text{BF}_3 \cdot \text{OEt}_2$ was performed in the presence of added ethylene gas in air, formation of $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ was also observed, but the yield did not exceed 5%.

It was established that the formation of $\text{C}_3\text{H}_3\text{NO}$ is not platinum-assisted, *i.e.* in a control experiment, treatment of nitromethane with either “aged” boron trifluoride-diethyl ether or freshly distilled $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of ethylene yielded isoxazole which was unambiguously identified by GC-MS. It is likely that platinum(II) coordinates the isoxazole as it is formed *in situ* and, hence, plays the rôle of an isoxazole-trapping reagent. The reaction in air of MeNO_2 and $\text{BF}_3 \cdot \text{OEt}_2$ in the presence of $\text{CH}_2=\text{CH}_2$ yielding isoxazole is novel. Other preparations of isoxazole derivatives utilizing *nitroalkanes* require basic conditions. Moreover, even under basic conditions, *nitromethane* does not give the expected isoxazole.⁴ A plausible pathway for the reaction described here includes deoxygenation of nitromethane followed by $[\text{CNO} + \text{CC}]$ oxidative cycloaddition with ethylene; as inert atmosphere conditions were not

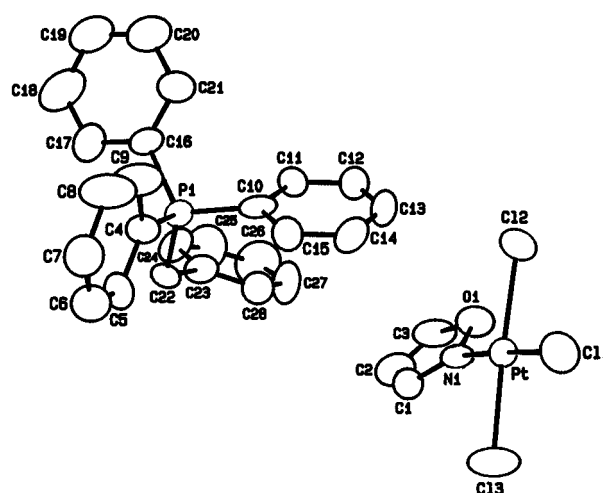


Fig. 1 Molecular structure of $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ (Polymorph I), with atom numbering scheme. Selected bond lengths (Å) and angles (°): Pt–Cl(1) 2.355(3), Pt–Cl(2) 2.276(3), Pt–Cl(3) 2.320(4), Pt–N(1) 1.92(1), Cl(1)–Pt–Cl(2) 88.3(1), Cl(1)–Pt–Cl(3) 87.1(1), Cl(1)–Pt–N(1) 175.6(3), Cl(2)–Pt–Cl(3) 175.3(1), Cl(2)–Pt–N(1) 94.8(3), Cl(3)–Pt–N(1) 89.9(3).

employed in this reaction, air oxidation may be involved. Work on determining the mechanism of this reaction and extensions to the synthesis of derivatives of isoxazole is under way, including experiments with nitroalkanes other than nitromethane and alkenes other than ethylene.

The complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ was also prepared by an independent route through reaction of commercially available isoxazole and $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ in DMF.¶ On slow evaporation of dichloromethane or mixed acetone–toluene solutions, the complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ crystallized in two polymorphic forms, I and II, respectively. Polymorph I was characterized by comparison of unit cell parameters with those of the previously characterized compound (I; see above) and polymorph II was independently characterized by X-ray crystallography.|| In each polymorph the compound consists of discrete ions, *i.e.* the phosphonium cation and the anion $[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]^-$. In the anion, the N atom and three Cl atoms form a slightly distorted square-plane around the Pt center. Bond lengths and bond angles of the isoxazole rings in I and II are comparable (within 3σ) and agree well with previously reported values for other isoxazole–metal complexes.⁵ The only significant differences in geometrical parameters between the two polymorphic forms is in the values of the Pt–Cl(*trans* to N) and Pt–N bond lengths. The complex $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$ is the first isoxazole complex of a platinum group metal to be structurally characterized.^{6,7}

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Notes and references

† Characterization of **A**. Yellow solid (Found: C, 56.4; H, 4.4; N, 1.1%); m/z (FAB⁺) 356; $\nu_{\max}/\text{cm}^{-1}$ 1083 vs and 1072 vs; 343 w and 330 m-w (Pt-Cl); ¹H and ¹³C{¹H} NMR spectra reveal no signals other than those due to the phosphonium cation even at high signal:noise ratios and this observation suggests that **A** is a phosphonium salt of a purely inorganic anion. All attempts to obtain X-ray quality crystals failed. Slow evaporation of a dichloromethane solution of **A** over *ca.* one month yielded only poor quality crystals. Dissolution of these crystals in CH₂Cl₂ and repeated slow evaporation gave only a few crystals of the well-known complex (Ph₃PCH₂Ph)₂[Pt₂(μ-Cl)₂Cl₄] (see ref. 2) along with additional poor quality, yellow crystals of **A**.

‡ "Aged" BF₃·OEt₂ (0.22 mL, 1.77 mmol) was added to a solution of (Ph₃PCH₂Ph)₂[PtCl₄]²⁻ (0.19 g, 0.18 mmol) in MeNO₂ (10 mL). After 30 min, the solvent was removed *in vacuo* at 40 °C. The oily residue was washed with Et₂O (30 mL), dissolved in MeOH (2 mL), filtered from small amounts of undissolved material and Et₂O (30 mL) was added to the filtrate. A precipitate formed which was collected on a filter and dried in air at 20–25 °C. Yields of (Ph₃PCH₂Ph)[PtCl₃(C₃H₃NO)] after column chromatography on SiO₂ (Wako; eluent CH₂Cl₂:Me₂CO = 2:1, *v/v*) were 10–15%. The isoxazole compound could also be separated from **A** on slow evaporation of a dichloromethane solution from a long narrow tube. The former is much less soluble in CH₂Cl₂ than the latter and crystals of (Ph₃PCH₂Ph)[PtCl₃(C₃H₃NO)] were separated by hand when they appeared in the upper part of the tube.

§ Characterization of (Ph₃PCH₂Ph)[PtCl₃(C₃H₃NO)] (i) sample obtained from MeNO₂-BF₃·OEt₂ synthesis (Calc. for C₂₈H₂₅Cl₃NOPPt: C, 46.46; H, 3.48; N, 1.93. Found: C, 45.62; H, 3.13; N, 1.87%); m/z (FAB⁺) 370 (Calc. 370 for [PtCl₃(C₃H₃NO)]⁺); mp 147–149 °C; (ii) sample obtained from independent synthesis (Calc. for C₂₈H₂₅Cl₃NOPPt: C, 46.46; H, 3.48; N, 1.93. Found: C, 46.53; H, 3.50; N, 1.87%); m/z (FAB⁺) 370 (Calc. 370 for [PtCl₃(C₃H₃NO)]⁺); mp 147–149 °C.

δ_{H} (CDCl₃, J values in Hz) (signals due to C₃H₃NO): 6.39 (dd, J_{HH} 2, 1H), 8.40 (d, J_{HH} 2, 1H) and 8.69 (d, J_{HH} 2, 1H); (signals due to Ph₃PCH₂Ph⁺): 5.18 (d, J_{PH} 14, 2H), 7.0–7.2 (m, phenyl protons, 8H), 7.6–7.8 (m, phenyl protons, 16H); δ_{C} ({¹H}, CDCl₃) (signals due to C₃H₃NO): 106.3, 149.4 and 158.8; $\nu_{\max}/\text{cm}^{-1}$ 1552 m (C=N), 336 s and 322 sh (Pt-Cl).

¶ Isoxazole (0.33 mL, 5.16 mmol; Aldrich) was added at room temperature to a solution of (Ph₃PCH₂Ph)₂[Pt₂(μ-Cl)₂Cl₄] (0.34 g, 0.26 mmol) in DMF (2 mL). The reaction mixture was left to stand for 3 h at 20–25 °C, then Et₂O (40 mL) was added to give an oily residue. After decanting of the solvent, methanol (3 mL) was added and the residue rapidly crystallized on stirring the mixture. The yellow precipitate was collected on a filter, washed twice with 1 mL portions of MeOH and three times with 3 mL portions of Et₂O, and dried in air at 20–25 °C. Yield of (Ph₃PCH₂Ph)[PtCl₃(C₃H₃NO)]: 0.19 g, 50%.

|| Crystal data for I: C₂₈H₂₅Cl₃NOPPt, $M_r = 723.94$; monoclinic, space group *Cc*, $a = 9.451(1)$, $b = 27.882(3)$, $c = 10.882(2)$ Å, $\beta = 106.55(1)^\circ$, $V = 2749(1)$ Å³, $D_c = 1.75$ g cm⁻³ for $Z = 4$, $F(000) = 1408$, radiation Mo-K α , $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 55.3$ cm⁻¹, $T = 294 \pm 1$ K, crystal size = 0.12 × 0.20 × 0.30 mm, mounted on a glass fibre, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $\omega - 2\theta$ scan technique, maximum $2\theta = 52.0^\circ$, unit cell constants from the setting angles of 25 reflections in the range $10 < \theta < 14^\circ$, Lorentz and polarization corrections, semi-empirical absorption correction based on a series of Ψ -scans (from 0.640–1.000 on I), anisotropic decay (from 0.961 to 1.030 on I), 2938 total reflections collected, 2938 unique, 2639 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, solution by direct methods,⁸ refinement by full-matrix least-squares, function minimized was $\Sigma w(|F_o| - |F_c|)^2$, weight w defined as $4F_o^2/\sigma^2(F_o^2)$, hydrogen atoms included with $U_{\text{iso}} = 1.3 \times U(\text{bonding atom})$, 314 refined parameters, $R = 0.035$, $R_w = 0.050$, $S = 1.77$, largest shift = 0.01 σ highest peak in final difference map 0.98 (15) e Å⁻³, low peak -0.23 (15) e Å⁻³. Scattering factors for neutral atoms and the values for $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography*;⁹ computer programs: MolEN.¹⁰

Crystal data for II: C₂₈H₂₅Cl₃NOPPt, $M_r = 723.94$; monoclinic, space

group *P2₁/c*, $a = 18.388(3)$, $b = 13.369(2)$, $c = 22.436(4)$ Å, $\beta = 95.41(1)^\circ$, $V = 5491(3)$ Å³, $D_c = 1.75$ g cm⁻³ for $Z = 8$, $F(000) = 2816$, radiation Mo-K α , $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 55.4$ cm⁻¹, $T = 294 \pm 1$ K, crystal size = 0.10 × 0.18 × 0.50 mm, mounted on a glass fibre, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $\omega - 2\theta$ scan technique, maximum $2\theta = 52.0^\circ$; unit cell constants from the setting angles of 25 reflections in the range $9 < \theta < 14^\circ$, Lorentz and polarization corrections, semi-empirical absorption correction based on a series of Ψ -scans (from 0.922–1.000 on I); anisotropic decay (from 0.965 to 1.069 on I), reflection averaging $R(\text{int}) = 2.1\%$, 11581 total reflections collected, 11219 unique, 6334 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, solution by direct methods,¹¹ refinement by full-matrix least-squares, function minimized was $\Sigma w(|F_o| - |F_c|)^2$, weight w defined as $4F_o^2/\sigma^2(F_o^2)$, hydrogen atoms included with $U_{\text{iso}} = 1.3 \times U(\text{bonding atom})$, 626 refined parameters, $R = 0.044$, $R_w = 0.053$, $S = 1.56$, largest shift = 0.01 σ , highest peak in final difference map 2.49 (14) e Å⁻³ (0.735 Å from Cl3), low peak 0.00 (15) e Å⁻³. Scattering factors for neutral atoms and the values for $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography*;⁹ computer programs: MolEN.¹⁰

Atomic coordinates, bond lengths and angles, and thermal parameters for I and II have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CDCC for this material should quote the full literature citation and the reference number 207/251.

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