

# 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,<sup>a</sup> Constanze Petersohn<sup>a</sup> and Vadim Yu. Kukushkin<sup>\*b</sup>

<sup>a</sup> Department of Chemistry, College of Arts and Sciences, University of Toledo, Toledo, Ohio 43606-3390, USA

<sup>b</sup> 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.<sup>1</sup> 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  $\text{CH}_2\text{Cl}_2$  or MeCN produces the chloride-bridged dimer  $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ <sup>2</sup> or the acetonitrile solvato-complex  $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{MeCN})]$ ,<sup>3</sup> 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  $\text{MeNO}_2$  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  $\text{SiO}_2$  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 <sup>1</sup>H NMR spectroscopy indicated the presence of  $\text{CH}_2=\text{CH}_2$  (5.40 ppm in  $\text{CDCl}_3$  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  $\text{MeNO}_2$  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.<sup>4</sup> 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

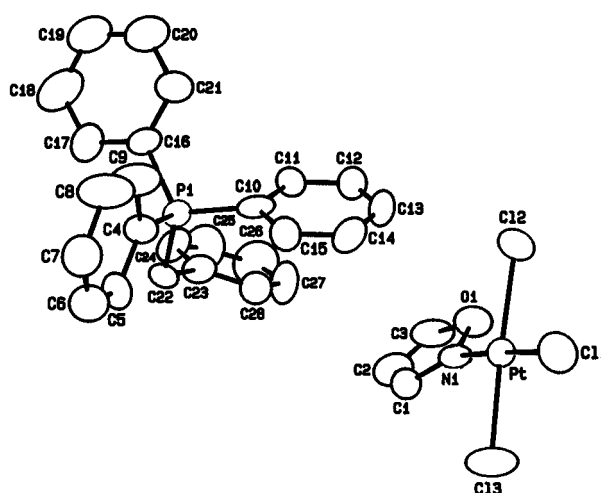


Fig. 1 Molecular structure of  $(\text{Ph}_3\text{PCH}_2\text{Ph})[\text{PtCl}_3(\text{C}_3\text{H}_3\text{NO})]$  (Polymorph I), with atom numbering scheme. Selected bond lengths (Å) and angles (°): Pt–Cl(1) 2.355(3), Pt–Cl(2) 2.276(3), Pt–Cl(3) 2.320(4), Pt–N(1) 1.92(1), Cl(1)–Pt–Cl(2) 88.3(1), Cl(1)–Pt–Cl(3) 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.<sup>5</sup> 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.<sup>6,7</sup>

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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<sup>+</sup>) 356;  $\nu_{\max}/\text{cm}^{-1}$  1083 vs and 1072 vs; 343 w and 330 m-w (Pt-Cl); <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} 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 CH<sub>2</sub>Cl<sub>2</sub> and repeated slow evaporation gave only a few crystals of the well-known complex (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>4</sub>] (see ref. 2) along with additional poor quality, yellow crystals of **A**.

‡ “Aged” BF<sub>3</sub>·OEt<sub>2</sub> (0.22 mL, 1.77 mmol) was added to a solution of (Ph<sub>3</sub>PCH<sub>2</sub>Ph)<sub>2</sub>[PtCl<sub>4</sub>]<sup>2</sup> (0.19 g, 0.18 mmol) in MeNO<sub>2</sub> (10 mL). After 30 min, the solvent was removed *in vacuo* at 40 °C. The oily residue was washed with Et<sub>2</sub>O (30 mL), dissolved in MeOH (2 mL), filtered from small amounts of undissolved material and Et<sub>2</sub>O (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 (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)] after column chromatography on SiO<sub>2</sub> (Wako; eluent CH<sub>2</sub>Cl<sub>2</sub>:Me<sub>2</sub>CO = 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 CH<sub>2</sub>Cl<sub>2</sub> than the latter and crystals of (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)] were separated by hand when they appeared in the upper part of the tube.

§ Characterization of (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)] (*i*) sample obtained from MeNO<sub>2</sub>-BF<sub>3</sub>·OEt<sub>2</sub> synthesis (Calc. for C<sub>28</sub>H<sub>25</sub>Cl<sub>3</sub>-NOPPt: C, 46.46; H, 3.48; N, 1.93. Found: C, 45.62; H, 3.13; N, 1.87%);  $m/z$  (FAB<sup>+</sup>) 370 (Calc. 370 for [PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)]<sup>+</sup>); mp 147–149 °C; (*ii*) sample obtained from independent synthesis (Calc. for C<sub>28</sub>H<sub>25</sub>Cl<sub>3</sub>-NOPPt: C, 46.46; H, 3.48; N, 1.93. Found: C, 46.53; H, 3.50; N, 1.87%);  $m/z$  (FAB<sup>+</sup>) 370 (Calc. 370 for [PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)]<sup>+</sup>); mp 147–149 °C.

$\delta_{\text{H}}$ (CDCl<sub>3</sub>,  $J$  values in Hz) (signals due to C<sub>3</sub>H<sub>3</sub>NO): 6.39 (dd,  $J_{\text{HH}}$  2, 1H), 8.40 (d,  $J_{\text{HH}}$  2, 1H) and 8.69 (d,  $J_{\text{HH}}$  2, 1H); (signals due to Ph<sub>3</sub>PCH<sub>2</sub>Ph<sup>+</sup>): 5.18 (d,  $J_{\text{PH}}$  14, 2H), 7.0–7.2 (m, phenyl protons, 8H), 7.6–7.8 (m, phenyl protons, 16H);  $\delta_{\text{C}}$ {<sup>1</sup>H}, CDCl<sub>3</sub> (signals due to C<sub>3</sub>H<sub>3</sub>NO): 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 (Ph<sub>3</sub>PCH<sub>2</sub>Ph)<sub>2</sub>[Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>4</sub>] (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 Et<sub>2</sub>O (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 Et<sub>2</sub>O, and dried in air at 20–25 °C. Yield of (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[PtCl<sub>3</sub>(C<sub>3</sub>H<sub>3</sub>NO)]: 0.19 g, 50%.

|| Crystal data for I: C<sub>28</sub>H<sub>25</sub>Cl<sub>3</sub>-NOPPt,  $M_r$  = 723.94; monoclinic, space group Cc,  $a$  = 9.451(1),  $b$  = 27.882(3),  $c$  = 10.882(2) Å,  $\beta$  = 106.55(1)°,  $V$  = 2749(1) Å<sup>3</sup>,  $D_c$  = 1.75 g cm<sup>−3</sup> for  $Z$  = 4,  $F(000)$  = 1408, radiation Mo-Kα,  $\lambda$  = 0.71073 Å,  $\mu$ (Mo-Kα) = 55.3 cm<sup>−1</sup>,  $T$  = 294 ± 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°, unit cell constants from the setting angles of 25 reflections in the range 10 <  $\theta$  < 14°, Lorentz and polarization corrections, semi-empirical absorption correction based on a series of  $\Psi$ -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,<sup>8</sup> 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 $\sigma$  highest peak in final difference map 0.98 (15) e Å<sup>−3</sup>, low peak −0.23 (15) e Å<sup>−3</sup>. Scattering factors for neutral atoms and the values for  $\Delta f'$  and  $\Delta f''$  were taken from *International Tables for X-ray Crystallography*;<sup>9</sup> computer programs: MolEN.<sup>10</sup>

Crystal data for II: C<sub>28</sub>H<sub>25</sub>Cl<sub>3</sub>-NOPPt,  $M_r$  = 723.94; monoclinic, space

group  $P2_1/c$ ,  $a$  = 18.388(3),  $b$  = 13.369(2),  $c$  = 22.436(4) Å,  $\beta$  = 95.41(1)°,  $V$  = 5491(3) Å<sup>3</sup>,  $D_c$  = 1.75 g cm<sup>−3</sup> for  $Z$  = 8,  $F(000)$  = 2816, radiation Mo-Kα,  $\lambda$  = 0.71073 Å,  $\mu$ (Mo-Kα) = 55.4 cm<sup>−1</sup>,  $T$  = 294 ± 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°, unit cell constants from the setting angles of 25 reflections in the range 9 <  $\theta$  < 14°, Lorentz and polarization corrections, semi-empirical absorption correction based on a series of  $\Psi$ -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,<sup>11</sup> 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 $\sigma$ , highest peak in final difference map 2.49 (14) e Å<sup>−3</sup> (0.735 Å from Cl3), low peak 0.00 (15) e Å<sup>−3</sup>. Scattering factors for neutral atoms and the values for  $\Delta f'$  and  $\Delta f''$  were taken from *International Tables for X-ray Crystallography*;<sup>9</sup> computer programs: MolEN.<sup>10</sup>

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.

- 1 J. A. Davies, C. M. Hockensmith, V. Yu. Kukushkin and Yu. N. Kukushkin, *Synthetic Coordination Chemistry: Principles and Practice*, World Scientific, Singapore–New Jersey–London, 1996.
- 2 V. Yu. Kukushkin, V. M. Tkachuk, I. A. Krol, Z. A. Starikova, B. V. Zhadanov and N. P. Kiseleva, *Zh. Obshch. Khim.*, 1991, **61**, 51.
- 3 V. Yu. Kukushkin, I. A. Krol, Z. A. Starikova and V. M. Tkachuk, *Koord. Khim.*, 1990, **16**, 1406.
- 4 W. R. Roush, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 5, p. 513; B. J. Wakefield and D. J. Wright, *Adv. Heterocycl. Chem.*, 1979, **25**, 147; N. K. Kochetkov and S. D. Sokolov, *Adv. Heterocycl. Chem.*, 1962, **2**, 365; S. A. Lang and Y.-I. Lin, in *Comprehensive Heterocyclic Chemistry*, ed. K. T. Potts, vol. 6, Pergamon Press, New York, 1984, p. 1; P. Grunanger and P. Via-Finzi, *Isoxazoles*, in *Chemistry of Heterocyclic Compounds*, vol. 49, part 1, Wiley Interscience, New York, 1991, pp. 877.
- 5 K. J. Oliver, T. N. Waters, D. F. Cook and C. E. F. Rickard, *Inorg. Chim. Acta*, 1977, **24**, 85; G. Pelizzi, *Transition Met. Chem.*, 1979, **4**, 199; C. K. Schauer, O. P. Anderson, N. R. Natale and D. A. Quincy, *Acta Crystallogr., Sect. C*, 1986, **42**, 884.
- 6 M. S. Munsey and N. R. Natale, *Coord. Chem. Rev.*, 1991, **109**, 251; a search of the *Cambridge Structural Database* revealed no other structural data of isoxazole complexes of the platinum group metals.
- 7 M. Biddau, G. Devoto, M. Massacesi and G. Ponticelli, *Transition Met. Chem.*, 1976, **1**, 99; I. A. Zakharova, Ja. V. Salyn, L. V. Tatjanenko, Yu. Sh. Mashkovsky and G. Ponticelli, *J. Inorg. Biochem.*, 1981, **15**, 89; G. Ponticelli, personal communication, 1997.
- 8 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. DeClerq and M. M. Woolfson, MULTAN80, University of York, UK, 1980.
- 9 *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, 1974 (Present distributor: Kluwer Academic Publishers, Dordrecht).
- 10 C. K. Fair, MolEN, *An Interactive Intelligent System for Crystal Structure Analysis*, User Manual, Enraf-Nonius, Delft, The Netherlands, 1980.
- 11 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, SIR, *J. Appl. Crystallogr.*, 1989, **22**, 389.

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