Reactions of chelated Pt^{II} and Pt^{III} imidoimino complexes: N-nitrosation involving transfer of an NO group from inorganic nitrites and nitrates

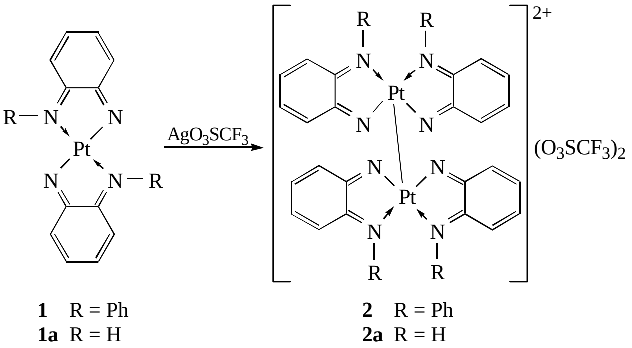
Marina O. Ponina, Aleksei A. Sidorov, Sergei E. Nefedov, Igor L. Eremenko* and Ilya I. Moiseev

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 952 1279; e-mail: ilerem@ionchran.msk.ru

A bis-chelated imidoimino Pt^{II} complex, $[(NPh)(N)C_6H_4]_2Pt$ **1**, was found to undergo N-nitrosation on reacting with $AgNO_2$ or $AgNO_3$ to form a product of formal HNO addition, $[(NPh)(NNO)C_6H_4][(NPh)(NH)C_6H_4]Pt$ **3**, that was characterised by X-ray analysis; similarly, an amidoimino binuclear Pt^{III} complex was converted into **3** by reacting with $NaNO_2$.

Bis-chelated Pt^{II} imidoimino complexes $[(NR)(N)C_6H_4]_2Pt$ (**1**, R = Ph; **1a**, R = H), having quinoid *trans*-NR-positioned ligands,[1,2] are known to react with AgO_3SCF_3 with formation of binuclear Pt^{III}–Pt^{III} diamagnetic compounds $\{[(NR)(N)C_6H_4]_2Pt\}^{2+}(O_3SCF_3)_2$ (**2**, R = Ph;[2] **2a**, R = H[3]) (Scheme 1).

Within the context of a program aimed at the investigation of coordinated imidoimino ligand reactivity we studied the interaction of the complexes **1** and **2** with inorganic nitrites and nitrates and observed N-nitrosation of the ligand leading to transfer of the NO group from NO_2^- and NO_3^- reagents under very mild conditions.

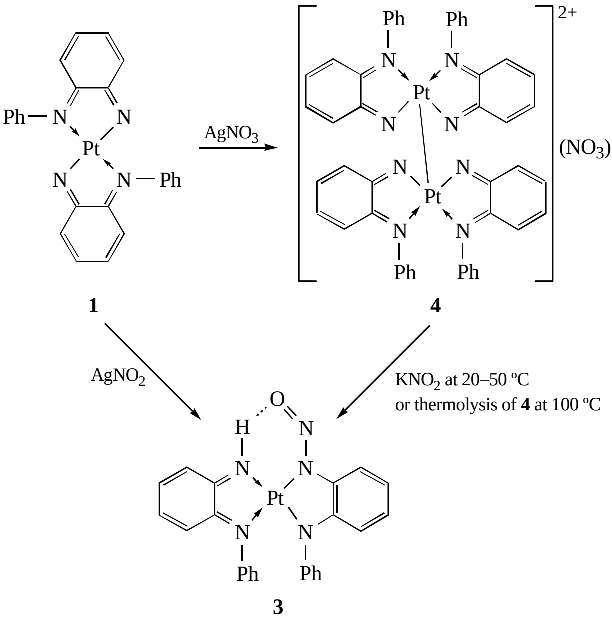


Scheme 1

No reaction between Pt^{II} complex $[(NR)(N)C_6H_4]_2Pt$ (**1**, R = Ph) and sodium nitrite/nitrate was observed at 20–60 °C in different solvents (THF, CH_2Cl_2, MeCN). However, **1** was found to react with $AgNO_2$ in THF (20 °C)† giving rise to complex $[(NPh)(NNO)C_6H_4][(NPh)(NH)C_6H_4]Pt$ **3** (Scheme 2). The reaction is accompanied by silver powder precipitation suggesting the involvement of a redox step in the process. Nevertheless, no formal change in the platinum atom oxidation state takes place in the course of the reaction.

A possible explanation for the facts observed could be the presence of an intermediate binuclear complex, an analogue of **2**, which is formed during the reaction. Within this proposal, complex **1** should first undergo oxidation by the Ag^+ in the $AgNO_2$ reagent to give a binuclear dication similarly to the oxidation **1** → **2** observed under the conditions where AgO_3SCF_3 is used as an oxidant.[2,3] Complex **2** is supposed to further react with NO_2^- ion giving rise to the observed product **3**. It is worth noting that complex **2** contains unusually long Pt–Pt distances [3.260(1) Å in **2** and 3.031(4) Å in **2a**, while the distance between the Pt^{II} atoms of the neighbouring molecules in the initial complexes **1** and **1a** is equal to 4.8 Å].

In order to verify this scheme, we studied the reaction of complex **2** with potassium nitrite. By reacting **1** and $AgNO_3$ in acetone at 20 °C a dimer of low solubility $\{[(NPh)(N)C_6H_4]_2Pt\}_2(NO_3)_2$ **4** was obtained‡ and the precipitation of metallic silver was observed. This complex reacts very easily at 20–50 °C with inorganic (KNO_2) nitrite under heterophasic conditions leading to complex **3**.‡ The data available are therefore consistent with the scheme assuming that the first stage of the reaction is the oxidation of Pt^{II} and formation of the dimers $\{[(NPh)(N)C_6H_4]_2Pt\}^{2+}X_2$, where $X = NO_2$ or NO_3. It should be noted that complex **4** also gives compound **3** and a new unidentified complex upon heating (100 °C, xylene). The binuclear complex **2** is stable at 100–140 °C. However, it reacts with KNO_2 at 50–80 °C forming complex **3** and the initial compound **1** in the ratio 1:2.



Scheme 2

---

† Complex **1** (200 mg, 0.36 mmol) was dissolved in 50 ml of THF to form a dark blue solution. Solid $AgNO_2$ (60 mg, 0.39 mmol) was added to the solution at 20 °C. The colour of the reaction mixture changed to brown-green in 30 min and the formation of grey metallic silver as an amorphous powder was observed. The solvent was removed at 25–30 °C (0.1 Torr) to dryness and the solid was extracted with diethyl ether (100 ml). The extract was filtered through a layer of silica gel (2×5 cm). The solution afforded brown prisms of **3** upon concentrating and cooling (–15 °C). Yield 89 mg (0.14 mmol, 39%). IR (KBr, ν/cm^{-1}) 1574 (m), 1487 (m), 1442 (m), 1392 (m), 1286 (m), 1256 (m), 1140 (m), 1064 (m), 920 (w), 907 (w), 870 (w), 832 (w), 802 (m), 742 (m), 688 (m), 658 (m), 598 (w), 588 (m), 564 (w). Found (%): C, 48.79; H, 3.01; N, 11.94. Calc. for $C_{24}H_{19}N_5OPt$ (%): C, 48.98; H, 3.23; N 11.90.

‡ Complex **1** (200 mg, 0.36 mmol) and $AgNO_3$ (65 mg, 0.38 mmol) were ground in an agate mortar with 2 ml of acetone. The resulting brown-black solid was extracted with chloroform (200 ml). After cooling of this brown solution to –18 °C a microcrystalline powder of **4** [115 mg, 0.09 mmol, 50%. Found (%): C, 22.98; H, 1.54, N, 6.76. Calc. for $C_{24}H_{18}N_6O_6Pt_2$ (%): C, 23.26; H, 1.45; N, 6.79.] was separated by decantation, washed with diethyl ether (10 ml) and dried *in vacuo*. Further reaction between **4** (100 mg, 0.08 mmol) and KNO_2 (25 mg, 0.16 mmol) in 2 ml of acetone was performed in the same manner affording 35 mg (0.06 mmol, 37.5%) of **3**. Complex **3** can also be prepared in one stage by the grinding of **1** with an excess of $AgNO_3$ and KNO_2 in 2–3 ml of acetone.

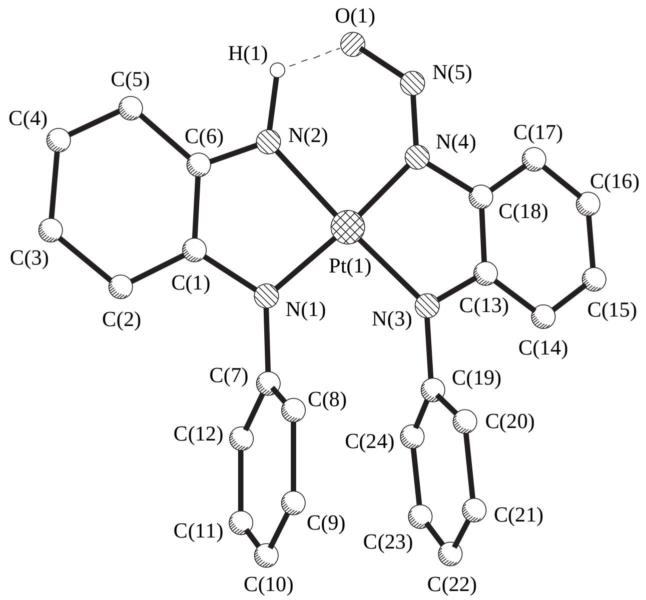


Figure 1 Crystal structure of compound **3**. Selected bond lengths (Å): Pt(1)–N(1) 2.027(8), Pt(1)–N(2) 1.973(9), Pt(1)–N(3) 1.981(8), Pt(1)–N(4) 2.004(8), O(1)–N(5) 1.303(16), N(1)–C(1) 1.367(14), N(1)–C(7) 1.436(14), N(2)–C(6) 1.325(14), N(3)–C(13) 1.403(14), N(3)–C(19) 1.434(14), N(4)–N(5) 1.338(14), N(4)–C(18) 1.429(14), C(1)–C(2) 1.412(15), C(1)–C(6) 1.443(16), C(2)–C(3) 1.358(17), C(3)–C(4) 1.412(19), C(4)–C(5) 1.342(17), C(5)–C(6) 1.435(17), C(13)–C(18) 1.385(16), C(14)–C(15) 1.403(17), C(15)–C(16) 1.401(19), C(16)–C(17) 1.379(19), C(17)–C(18) 1.374(16); selected bond angles (°): N(1)–Pt(1)–N(2) 79.1(3), N(1)–Pt(1)–N(3) 104.4(3), N(2)–Pt(1)–N(3) 176.3(4), N(1)–Pt(1)–N(4) 175.4(4), N(2)–Pt(1)–N(4) 96.4(4), N(3)–Pt(1)–N(4) 80.1(3), Pt(1)–N(4)–N(5) 132.1(8), O(1)–N(5)–N(4) 115.5(10).

The monomeric and diamagnetic compound $[(NPh)(NNO)C_6H_4][(NPh)(NH)C_6H_4]Pt$ **3** contains a Pt^{II} atom, as in starting compound **1**. According to the X-ray data[§] (Figure 1), the phenyl substituents of the ligands in **3** [C(Ph)–N 1.43(1) and 1.44(1) Å; the N atoms of the NPh moieties for both ligands have a trigonal-planar configuration] are *cis*-positioned, unlike the *trans*-configuration of these groups in the starting material. The H atom and NO group are attached to another two N atoms of molecule **3** [N–H distance 1.09(5) Å; the NNO fragment has a bent configuration with distances N–N 1.34(1) Å, N–O 1.30(2) Å, ∠N–N–O 115(1)°]. The NH and NNO groups are bound together *via* a hydrogen bond H···O [1.76(3) Å] to form a six-membered metallacycle. The N–O and N–N bond distances in the N–N=O group are in the range between single and double bonds probably indicating the delocalisation of the electron density over this fragment. It is interesting to note that the interatomic distances in the chelate $(NPh)(NNO)C_6H_4$ group of **3** are close to those expected for the benzoid form [N(Ph)–C(C_6H_4) 1.40(1) Å, N(NO)–C(C_6H_4) 1.43(1) Å]. Meanwhile, the ligand moiety with the protonated group $(NPh)(NH)C_6H_4$ features a quinodiimine geometry [N(Ph)–C(C_6H_4) 1.37(1) Å, N(H^+)–C(C_6H_4) 1.32(1) Å, a six-membered carbon ring containing two short and four long C–C bonds (see Figure 1)]. In addition, the metal-to-metal distance in **3** is obviously non-bonding [Pt···Pt length for the neighbouring molecules is equal to 4.947(1) Å]. The mechanistic aspects of the reactions will be discussed in a full paper.

We are thankful to the Russian Foundation for Basic Research (grant no. 96-03-33171) for financial support. The X-ray structural investigation was performed at the X-Ray Structural Centre (INEOS, RAS).

References

1 A. A. Sidorov and S. B. Katser, *Zh. Neorg. Khim.*, 1994, **39**, 860 (*Russ. J. Inorg. Chem.*, 1994, **39**, 900).
2 I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. O. Ponina, P. V. Danilov, T. A. Stramnova, I. P. Stolarov, S. B. Katser, S. T. Orlova, M. N. Vargaftik, I. I. Moiseev and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1998, **551**, 171.
3 A. A. Sidorov, M. O. Ponina, S. E. Nefedov, I. L. Eremenko, Yu. A. Ustynyuk and Yu. A. Lusikov, *Zh. Neorg. Khim.*, 1997, **42**, 853 (*Russ. J. Inorg. Chem.*, 1997, **42**, 952).
4 F. A. Allen, O. Kennard, D. G. Watson, L. Brammer, A. Guy Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

Received: Moscow, 5th August 1998
Cambridge, 11th September 1998; Com. 8/06232C

[§] Rhombohedral crystals, space group *R*3, a = 22.970(3), c = 21.594(4) Å, V = 9867(5) Å^3, Z = 18, R_1 = 0.042, R_w = 0.058 for 2315 reflections with $F > 4.0\sigma$. Bond lengths, bond angles, atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to authors’, *Mendeleev Communications*, 1998, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/29.