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Interplay between nitronates and nitriles accomplished in a Pt^{IV}-mediated reaction

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ABSTRACT

Reaction between the coordinated propanenitriles in *trans*-[PtCl₄(EtCN)₂] and the cyclic nitronate $ON=CHCH(C_6H_4OMe)CH_2CMe_2O$ (1) gives the *N*-acylated iminocomplex [PtCl₄{N(CEtO)=CHNOCH(C₆H₄OMe)CH₂CMe₂}] (2) which is unstable in wet solvents and undergoes hydrolysis to furnish [PtCl₄{NH=CHNOCH(C₆H₄OMe)CH₂CMe₂}] (3). The formulation of 2 and 3 was supported by satisfactory C, H, and N elemental analyses, agreeable HRESI⁺-MS, IR, ¹H NMR spectroscopies, and single-crystal X-ray diffraction (for *trans*-3).

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In view of our general interest in conversions of metal-activated substrates, in the past decade we had focused our attention on reactions of ligands bearing the CN triple bond, *i.e.* RCN and RNC species, toward coupling [1] or cycloaddition (CA) [2] and this topic has been surveyed by some of us [1a–d,2a–d,f–h] and others [1e–m,2e]. Our experimental [2b–d,2f–h] and theoretical [3] results demonstrate that the coordination of RCN to platinum centers dramatically enhances the reactivity of the nitriles toward dipoles of both allyl- (*e.g.*, open chain **A** and cyclic nitrones **B** [2b–d,2h]; Fig. 1) and propargyl/allenyl (*e.g.* nitrile oxides **C** [2f,2g]) anion types in comparison with 1,3-dipolar cycloaddition to free RCN molecules. In particular, nitriles coordinated to a Pt^{IV} center undergo CA with aromatic and aliphatic nitrones [2a–c] under mild conditions that are not accessible in metal-free organic syntheses.

Being interested in extension of the Pt-mediated CA reactions of nitriles to other dipoles, we launched a project aimed to verify, by theoretical methods, various factors affecting CA and found [3a,3b] that the reactivity of nitronates (**D**; Fig. 1) toward RCN is expected to be lower than that for the previously investigated acyclic (**A**) [2b–d] and cyclic nitrones (**B**) [2e–h]. Supporting in a collateral way our data [3a,b], up to now *Chemical Abstracts* give no even a

single reference relevant to reaction between either complexed or uncomplexed nitrile species and nitronates.

Bearing in mind the theoretical results outlined in the previous paragraph, we attempted to react nitronate **1** (Fig. 2; IUPAC [4] name: 4-(4-methoxy-phenyl)-6,6-dimethyl-5,6-dihidro-4H-[1,2] oxazin-2-oxide) with EtCN in *trans*-[PtCl₄(EtCN)₂] insofar as it was previously demonstrated that the ligation of nitriles to a Pt^{IV} center ought to provide even a higher activation effect upon cyclo-addition in comparison with the introduction of such powerful electron-acceptor group R as CF₃ to RCN [3]. To our knowledge, this report covers the first example of any reaction between a nitronate and a nitrile and it makes known that the interaction becomes possible in a metal-mediated reaction.

The starting material, *trans*-[PtCl₄(EtCN)₂], was obtained by the known procedure [5], and nitronate **1** (Scheme 1) was synthesized from β -nitro-4-methoxystyrene and isobutylene by the literature method [6]. Reaction between *trans*-[PtCl₄(EtCN)₂] and **1** proceeds at room temperature for 12 h and gives *N*-acylimine complex **2** as the major product, when the synthesis was carried out in freshly distilled CH₂Cl₂ [7]. Compound **2** is found to be unstable in air and in wet solvents and it is hydrolyzed to form imine complex **3**. The latter can be alternatively synthesized from *trans*-[PtCl₄(EtCN)₂] and **1** in moderate yield if the reaction was performed in nondried solvents [8].

Compounds **2** and **3** give satisfactory C, H, N elemental analyses and were also characterized by HRESI⁺-MS, IR, and ¹H NMR spectroscopies; the structure of **3** was determined by X-ray crystallography.



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Fig. 1. Schematic representation of open chain (A) and cyclic (B) nitrones, nitrile oxides (C), and nitronates (D).

Complex 2 has the same brutto-formula, *i.e.* C₃₂H₄₄N₄O₆Cl₄Pt, as the product derived from the cycloaddition of 1 to trans-[PtCl₄(EtCN)₂]. Hence, the elemental analyses and HRESI⁺-MS support only the composition of 2 and its structure should be verified by physicochemical methods. The IR spectrum of 2 shows no band(s) assignable to $v(C \equiv N)$ vibrations, but the observation of two strong stretches at 1746 and 1615 cm⁻¹ that were attributed to v(C=0) and v(C=N), respectively. In the ¹H NMR spectrum of 2, the ABX system [2.24 dd (12.5 and 8.1 Hz), 2.61 dd (12.5 and 9.2 Hz), and 5.30 t (8.4 Hz)] is recognized. This NMR pattern gives one of the evidences favoring the contraction of the six-membered ring to furnish the isoxazolidine. In **2**, the former 2-H proton from the nitronate cycle does not exhibit indirect spin-spin interactions with the other protons, but shows the coupling from ¹⁹⁵Pt and its signal appears as a singlet flanked with two satellites (³J_{PtH} 28.9 Hz). The signals from the Et group are manifested as two broad multiplets; this broadening relates, presumably, to a slow rotation of the C(=O)Et moiety around the NC bond. All these characteristic features of the ¹H NMR spectrum along with the IR data confirm the formulation of **2** as the *N*-acylimine complex rather than the cycloaddition product.

The IR spectrum of **3**, in contrast to **2**, displays a medium-tostrong band at 3380 cm^{-1} that corresponds to v(NH) vibrations; the C=N stretches are displayed at slightly higher wave numbers



Fig. 2. Thermal ellipsoid view of **3** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. One of the two forms having different stereochemical configuration at the C6 atom is given. Selected bond lengths [Å] and angles [°]: Pt(1)–N(1) 2.014(5), Pt(1)–Cl(1) 2.332(5), Pt(1)–Cl(2) 2.301(4), N(1)–C(1) 1.259(11), N(2)–C(1) 1.335(12), O(1)–N(2) 1.357(7); N(1)–Pt(1)–Cl(2) 91.6(6), N(1A)1–Pt(1)–Cl(2) 88.6(5), N(1)–C(1)–N(2) 125.4(13).

(1664 cm⁻¹) than in **2**. In the ¹H NMR spectrum, one can observe the ABX system characteristic for the 2,3,5,5-substituted isoxazolidine ring; the signal of the CH proton from the amidine fragment appears as a doublet flanked with satellites due to the coupling of the NH proton from the amidine group with ¹⁹⁵Pt.

Complex **3** was crystallized in non-centrosymmetrical space group *C*² and it lies in a special position at the twofold axis that passed through the metal center perpendicular to N1–N1A line and through the centroids between the Cl1…Cl1A and Cl2…Cl2A



Scheme 1.



Scheme 2.



Scheme 3.

atoms [9]. The complex has a pseudo-center of symmetry (at the Pt atom), which, in general, disturbed by the chiral C6 atom. Insofar as position of the heavy atoms in the structure obeys the centro-symmetrical law, it is not possible to determine unambiguously an absolute configuration of the complex (Flack parameter is 0.44(2)). However, the crystallography data give evidences that two centers (C6 and C6A in both heterocyclic ligands) display the same configuration, *i.e. RR* or *SS*.

A plausible mechanism for the observed conversion involves CA of **1** to platinum(IV)-activated EtCN's followed by the ring opening of 2,3-dihydro-1,2,4-oxadiazole ring and concomitant contraction of the 1,2-oxazinane cycle (Scheme 2).

Some works describe the ring opening of 2,3-dihydro-1,2,4-oxadiazoles that proceeds *via* the N–O bond cleavage accompanied by decarboxylation [10] or H-migration in free [11] or Pt-coordinated heterocycle [12] to furnish *N*-acylimines. Other recently reported transformation of 2,3-dihydro-1,2,4-oxadiazoles bearing electronacceptor substituents R with aryl migration onto amino-N (Scheme 3) looks rather similar to the rearrangement described in Scheme 2 [13].

These literature data favor the CA mechanism of the interaction between the complexed EtCN and the nitronate suggested in this work.

We succeeded so far to achieve the interaction between one relatively stable nitronate and one rather well soluble nitrile platinum precursor. In other cases, poor solubilities of the [PtCl₄(RCN)₂] (R = Me, CH₂Ph, Ph) complexes in dry dichloromethane on one hand and limited stability or low reactivity of other nitronates (e.g., $ON=CMeCH(C_6H_5)CH_2CMe_2O$, MeCH=N(O)OSiMe₃, EtCH=N(O)OSiMe₃,) on the other hand led to unselective processes and determined generation of broad spectra of products with no major components. Further works on reactions between nitronates and complexed nitriles are underway in our group.

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Appendix A. Supplementary material

CCDC 705255 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2008.12.006.

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- [7] Compound 1 (131 mg, 0.560 mmol) was added to a stirred suspension of trans-[PtCl₄(EtCN)₂] (100 mg, 0.224 mmol) in dry CH₂Cl₂ (5 mL), whereupon a vellow solution was formed within 10-15 min. The reaction mixture was stirred at room temperature for 12 h, then the volume was reduced to half of its initial volume by vacuum evaporation at room temperature and Et₂O (10 mL) was added. Yellow powder formed was filtered off, washed with dry Et₂O (two 5-mL portions) and dried on air. Yield is 112 mg, 54%. Additional amount of the solid complex (25 mg, 12%) can be obtained after vacuum evaporation of the filtrate and treatment of the yellow oily residue with Et₂O (15 mL). NMR yield ca. 95%. Compound 2. Anal. Calcd for C₃₂H₄₄N₄O₆Cl₄Pt · ¹/₄CH₂Cl₂: C, 41.26; H, 4.78; N, 5.97. Found C, 41.25; H, 4.90; N, 5.93 (the solvated dichloromethane was observed in the ¹H NMR spectrum). HRESI*-MS, m/z: 847.225 [M-2Cl+H]⁺ (847.231 calcd.). IR (KBr, selected bands, cm⁻¹): 2977 m, 2836 m-w v(C-H), 1746 m-s, br v(C=O), 1615 s, br v(C=N), 1253 m ν(C-O). ¹H NMR (CDCl₃, δ): 1.13 (t, br, 7.73 Hz, 3H, CH₃ from Et), 1,43 (s, 3H, Mea), 1.49 (s, 3H, Mee), 2.24 (dd, 12.5 and 9.2 Hz, 1H), 2.61 (dd, 12.5 and 8.1 Hz, 1H)(CH2), 2.93 (m br, 2 H, -CH2 from Et), 3.82 (s, 3H, OMe), 5.30 (t, 8.4 Hz, 1H, CH–Ar), 6.92 (d, 8.7 Hz, 2*H*, o- or *m*-Ph), 7.21 (d, 8.7 Hz, 2*H*, o- or *m*-Ph), 7.67 (s + d, 1H, ³J_{PtH} 28.9 Hz, CH=N). ¹³C NMR (CD₂Cl₂, δ): 8.1 and 35.6 (Et), 24.9 and 25.3 (Mea and Mee), 48.0 (CH2), 55.2 (MeO), 66.5 (CH-Ar), 87.5 (CMe2), 114.6 (m-Ar), 127.5 (Cipso), 128.4 (o-Ar), 146.8 (CH=N), 160.4 (p-Ar), 182.1 (C=O).
- [8] Complex **3** was prepared by the method described for **2** but wet solvents $(CH_2Cl_2 \text{ and } Et_2O)$ were used instead of the dried and freshly distilled. The dark-brown reaction mixture after stirring for 12 h was evaporated until dryness, and the formed brown oily residue was treated with Et_2O (3 × 3 mL). The brown-orange solid thus obtained was recrystallized twice from a $CH_2Cl_2/$ Et_2O mixture and the orange-yellow powder of **3** was obtained in *ca*. 20% yield. Complex **2** is unstable in solutions of the most common commercially available deuterated solvents and slowly hydrolyzed to furnish **3** with NMR yield after 3 days at room temperature in nondried $CDCl_3$ *ca*. 90%. Compound **3**. Anal. Calcd for $C_{26}H_{36}N_4O_4Cl_4Pt$: C, 38.77; H, 4.50; N, 6.96. Found C, 38.91; H, 4.62; N, 6.68. HRESI⁺-MS, *m*/*z*: 844.064 [M-H+K]⁺ (844.065 calcd.). IR (KBr,

selected bands, cm⁻¹): 3380 m v(N–H), 2973 m v(C–H), 1664 s, br v(C=N), 1251 m v(C–0), ¹H NMR (CDCI, δ): 1.45 (s, 3H, Me₂), 1.53 (s, 3H, Me_e), 2.26 (dd, 9.2 and 12.5 Hz, 1H), 2.63 (dd, 8.2 and 12.5 Hz, 1H)(CH₂), 3.82 (s, 3H, OMe₂), 5.20 (t, 8.60 Hz, 1H, CH-Ar), 6.02 (d, br, J_{HH} 14.4 Hz, 1H, NH), 6.92 (d, 8.4 Hz, 2H, o- or m-Ph), 7.22 (d, 8.8 Hz, 2H, o- or m-Ph), 7.38 (d + satellites, 1H, J_{PH} 28.6 Hz, ³J_{HH} 14.7 Hz, CH=N). ¹³C NMR was not measured due to low solubility of the complex in CDCl₃. Orange-yellow crystals of **3** suitable for X-ray diffraction study were obtained by slow (1 week) evaporation of solution of **2** in nondried CDCl₃.

- [9] X-ray Crystal Structure Determinations. Crystal data for **3**: $C_{26}H_{36}Cl_4N_4O_4Pt$, M = 805.48, $0.19 \times 0.09 \times 0.06 \text{ mm}^3$, monoclinic, space group C2, a = 16.123(3), b = 10.527(2), c = 11.082(2)Å, V = 1560.7(5)Å³, Z = 2, $D_c = 1.714$ g/cm³, $\mu = 4.875$ mm⁻¹, $F_{000} = 796$, Bruker SMART APEX II diffractometer, MoK α radiation, $\lambda = 0.71073$ Å, T = 100(2) K, $2\theta_{max} = 56^\circ$, 5826 reflections collected, 3734 unique ($R_{int} = 0.0403$). The APEX II software [APEX II software package, Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI 5317, 2005] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL [SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998] for space group and structure determination, refinements, graphics, and structure reporting. The refinement converged to $wR_2 = 0.0912$ and GOF = 1.043 (refinement on F^2 for all independent reflections, and $R_1 = 0.0462$ (refinement on F for 3309 observed reflections with $I > 2\sigma(I)$), 169 refined parameters.
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