Note

Iminoacylation

2. Addition of alkylated hydroxylamines via oxygen to platinum(IV)-bound nitriles

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Abstract

Addition of R2NOH (R = Me, Et, CH2Ph) to the acetonitrile ligands in the platinum(IV) complex trans-[PtCl4(MeCN)2] leads to unprecedented O-iminoacylation of the dialkylhydroxylamines to produce trans-[PtCl4(NH(Me)C(ONR2)]2. © 1999 Elsevier Science S.A. All rights reserved.

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Hydroxylamine is an ambidentate nucleophile and its N- and O-additions to the nitrile group are known [1–4]. It is well documented in organic chemistry that in the overwhelming majority of cases NH2OH adds to RC≡N via its nitrogen and this reaction leads to generation of amide oximes, RC(NH2)=NOH, through intermediate formation of RC(=NH)NHOH [1–4]. Strong acceptors R in RC≡N make the nitrile carbon increasingly susceptible to nucleophilic attack by more electronegative oxygen—rather than by a nitrogen atom—and conventional N-additions are accompanied by less usual O-additions giving, in the latter case, carboxamides RC(=O)NH2 along with NH3 and N2 [1–6].

To the best of our knowledge, the addition of NH2OH to coordinated RCN species or vice versa has not yet been investigated, whereas the addition of oximes (R'C≡NOH) have been reported recently by us [7]. However, there are two examples of metal-mediated additions of alkylated hydroxylamines to organonitriles. Wieghardt et al. in their pioneering work [8] reported on the reaction between [MoO2(MeNHO)2] and MeCN in the presence of MeNHOH·HCl, which furnishes the complexes ligated by a N,N'-NH=[(Me)C–N(O−)Me ligand (A in Fig. 1). Most likely the tendency for the N-additions of hydroxylamines is so strong that when WO2Cl2 was treated with Et2NOH

Fig. 1.

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in MeCN the reaction yielded \([\text{WO}_2\{\text{N,O}}\-

\text{NH=}(\text{Me})\text{C}--\text{N}(\text{Et})\text{O}\}_2]\) (B in Fig. 1) due to dealkylation/N-addition reactions [9].

These observations indicate that a hydroxylamine can be added to a coordinated nitrile at a metal center, although in quite a different way from the nucleophilic O-addition of oximes that we have already established [7]. Hence, with the aim to compare the behavior of hydroxylamines and oximes, and eventually establishing a novel type of reactivity for the former compounds, we investigated the reactions of dialkylhydroxylamines \(R_2\text{NOH}\) (\(R = \text{Me, Et, CH}_2\text{Ph}\)) with \(\text{trans-}[\text{PtCl}_4(\text{MeCN})_2]\). The acetonitrile ligands are highly electrophilically activated [7,10] by coordination to the quadruple charged platinum(IV) center, and, in contrast to the above-mentioned addition of Et\(_2\)NOH to acetonitrile in the tungsten-mediated system [9], the reaction of the Pt(IV) complex in MeCN proceeds in an unusual direction giving the O-iminoacetylated dialkylhydroxylamine complex \(\text{trans-}[\text{PtCl}_4(\text{NH}-(\text{Me})\text{C}-\text{O})\text{NR}_2)_2]\) in good (\(R = \text{CH}_2\text{Ph}\)) to almost quantitative (\(R = \text{Me or Et}\)) yield (Scheme 1).

The structure of \(\text{trans-}[\text{PtCl}_4(\text{NH}=-(\text{Me})\text{C}--\text{ONEt}_2)_2]\) was determined by X-ray single-crystal diffraction. The coordination polyhedron of the complex is a slightly distorted octahedron (Fig. 2).

The Pt atom is situated at an inversion center and the two iminoacyl ligands are mutually trans. All bonds and angles are of normal values [7,11,12]. The data obtained indicate intramolecular hydrogen bonding between the imino hydrogen and uncoordinated hydroxylamine nitrogen, e.g. distances N(1)⋯N(2), N(1)--H, H⋯N(2) are 2.60, 0.79 and 2.10 Å, respectively; N(1)⋯H⋯N(2) angle is 121°. Comparison of these distances with typical N⋯N (2.94–3.15 Å) and H⋯N (2.20 Å) ones in case of NH⋯N bonding [13] and also with the sum of the van der Waals radii for H and N (1.20 + 1.55 = 2.75 Å [14]) gives additional evidence in favor of the hydrogen bond.

It is worthwhile to mention that diethylhydroxylamine selectively reacts with the coordinated nitriles in \(\text{trans-}[\text{PtCl}_4(\text{MeCN})_2]\) rather than with free acetonitrile (a solvent for the reaction), despite incomparably higher concentration of the latter. Furthermore, \(^1\text{H}\) NMR experiment shows that Et\(_2\)NOH does not react with acetonitrile under the reaction or even more harsh (56°C, 10 days) conditions and this gives an additional argument in favor of a metal-mediated pathway for the process. However, the reaction of \(\text{PhCH}_2\text{OHNOH\text{MeCN}_2}\) with \(\text{trans-}[\text{PtCl}_4(\text{MeCN})_2]\) in acetonitrile led not only to the O-iminoacylated complex but also to a broad spectrum of products which were not separated. In addition, our attempts to carry out similar reactions with NH\(_2\)OH failed. Stirring \(\text{trans-}[\text{PtCl}_4(\text{MeCN})_2]\) and hydroxylamine (obtained by reaction of NH\(_2\)OH·HCl and Na\(_2\)CO\(_3\) in acetonitrile) in both MeCN and MeOH resulted in an overall darkening of the reaction mixtures and, eventually, gave a mixture of unidentified products. Treatment of \(\text{trans-}[\text{PtCl}_4(\text{MeCN})_2]\) with NH\(_2\)OH·HCl in MeCN in the absence of a base led to the reduction of the platinum(IV) center to afford the previously described [15] \([\text{PtCl}_2(\text{MeCN})_2]\).

![Scheme 1.](image1)

![Fig. 2. ORTEP drawing of trans-[PtCl4(NH-(Me)C-ONEt2)2] with atomic numbering scheme. Selected distances (Å) and angles (°): O–C(1) 1.346(6), O–N(2) 1.477(5), N(1)–C(1) 1.279(6), N(2)–C(5) 1.470(8), N(2)–C(3) 1.474(8), C(1)–C(2) 1.462(10); C(1)–N(1)–Pt 135.5(4), N(1)–C(1)–O 120.4(5), C(1)–O–N(2) 113.5(4).](image2)
In conclusion, we have achieved high selectivity towards the yet unusual nucleophilic O-addition of some hydroxylamines to the nitrile ligand activated by coordination to a Pt(IV) center. However, the reaction is dependent on a variety of factors (which include the type of hydroxylamine used) and its full understanding requires further systematic investigations. Hence, studies on additions of other hydroxylamine derivatives, e.g., monoalkylated hydroxylamines, ketoximes, aldoximes, vic-dioximes and hydroxamic acids, to coordinated organonitriles and cyanamides—with the aim of developing the chemistry of iminoacylation of hydroxylamine derivatives—are in progress by our group.

1. Experimental

1.1. Materials and instrumentation

All instruments used have been described in Ref. [7].

1.2. Synthesis and characterization

1.2.1. trans-[PtCl4(NH-(Me)CONMe2)]

Me2NOH·HCl (24.5 mg, 0.2 mmol) was stirred with Na2CO3 (28 mg, 0.2 mmol) in dichloromethane (10 ml) for 30 min at 20–25°C and the suspension was filtered. trans-[PtCl4(MeCN)] (42 mg, 0.1 mmol) was added to the filtrate and the reaction mixture was stirred for 3 h at room temperature until homogenization was complete and then the solution was passed through a 3 cm column filled with Silicagel (Merck, Kieselgel 60) and the solvent was removed by evaporation. Yield: 96%.

1.2.2. trans-[PtCl4(NH-(Me)CONMe2)]

The complex was prepared by the reaction of trans-[PtCl4(MeCN)] (0.15 g, 0.25 mmol) and Et3NOH (0.62 mmol) in acetonitrile (7 ml) at 20–25°C for 1 day followed by removal of the solvent in vacuo and careful washing of the precipitate with Et2O. Yield: 96%. Anal. Calc. for C12H38N4Cl4O2Pt: C, 17.86; H, 3.73; N, 6.4. Found: C, 17.87; H, 3.7; N, 6.5. FAB +-MS, m/z: 505 [M – Cl]–, 570 [M – 2Cl]–. M.p. = 175°C. TLC on Silufol UV 254 F254 SiO2 plates: Rf = 0.44 (elucent CHCl3). IR spectrum in KBr, selected bands, cm⁻¹: 3244 m ν(N–H), 1656 s ν(C=N), 1H NMR in CDCl3, δ: 2.59 (s + d, J_HH 3.8 Hz, 3H, =CMe), 2.82 (s, 6H, NMe2), 13C{1H} NMR in CDCl3, δ: 17.9 (Me), 47.6 (NMe2), 174.3 (C=N). 195Pt NMR in CDCl3, δ: −165 (700 Hz).

1.2.3. trans-[PtCl4(NH-(Me)CON(CH2Ph)]

The complex was prepared by the reaction of trans-[PtCl4(MeCN)] (42 mg, 0.1 mmol) and (PhCH2)2NOH (53 mg, 0.2 mmol) in CH2Cl2 (2 ml) at 20–25°C for 3 h and chromatography of the reaction mixture on SiO2/CH2Cl2, followed by removal of the solvent in vacuo. Yield: 62%. Anal. Calc. for C32H36N4Cl4O2Pt: C, 45.5; H, 4.3; N, 6.6. Found: C, 45.7; H, 4.3; N, 6.4. FAB +-MS, m/z: 809 [M – Cl]–, 774 [M – 2Cl]–, 738 [M – 3Cl – H]–. M.p. = 142°C. TLC on Merck 60 F254 SiO2 plates: Rf = 0.74 (elucent CH2Cl2). IR spectrum in KBr, selected bands, cm⁻¹: 3244 m ν(N–H), 1656 s ν(C=N), 1H NMR in CDCl3, δ: 2.42 (s + d, J_HH 3.8 Hz, 3H, =CMe), 4.09 (d, J_HH 12.9 Hz, 2H) and 4.15 (d, J_HH 12.9 Hz, 2H) (CH2Ph), 7.37 (m, 10H, Ph), 9.07 (s, br, NH). 13C{1H} NMR in CDCl3, δ: 17.3 (Me), 61.9 (CH2Ph), 128.5, 129.0, 129.8 and 133.3 (Ph), 174.2 (C=N). 195Pt NMR in CDCl3, δ: −166 (710 Hz).

1.3. Crystal data

C12H38N4Cl4O2Pt, M = 597.27, orthorhombic, space group Pbc a, a = 8.630(4), b = 13.438(3), c = 18.140(2) Å, U = 2103.7(11) Å³, Z = 4, Dcalc = 1.886 g cm⁻³, T = 293(2) K, β-filtered Mo–Kα radiation, λ = 0.71073 Å, F(000) = 1160, bright yellow plates with dimensions 0.40 × 0.31 × 0.07 mm, μ(Mo–Kα) = 7.189 mm⁻¹, numeric absorption correction, transmission factors 0.159–0.589, CAD-4 diffractometer, collection method θ/2θ, data collection range 2.25 ≤ θ ≤ 24.96°, index ranges −10 ≤ h ≤ 0, 0 ≤ k ≤ 15, 0 ≤ l ≤ 21, three standard reflections showed no significant variation in intensity, 1965 independent reflections collected (Rint = 0.0), numeric absorption correction applied on a ‘faced’ crystal using procedure given in SHELXL-91 [16], the structure was solved by a heavy atom method and the refinement was done by full-matrix-block least-squares on F² (SHELXL-93 program) [17], refined H atoms, 840 data (with I > 2σ(I)), 0 restraints, 164 parameters, final R indices (observed data) R1 = 0.0167, wR2 = 0.0416, GoF = 1.080, largest difference peak = 0.679 e Å⁻³ located 0.96 Å from the Pt atom.

2. Supplementary material

Crystal data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and are available upon request on quoting the deposition number CSD-115331.
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References