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A vanadium-promoted C–N bond cleavage

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Abstract

A C–N bond in one arm of the mixed-valence V^{III}–V^{IV} complex bpbp($VOCl_2$)(VCl_2), bpbpH = 2,6-bis((*N*,*N*-bis-(2-picolyl)amino)-methyl)-4-tertbutylphenol, is cleaved in wet acetonitrile solution to give bpa($VOCl_2$), bpa = bis(2-methypyridyl)amine, and 2-((*N*,*N*-bis-(2-picolyl)amino)methyl)-6-hydroxymethyl-4-tertbutylphenol. The reaction corresponds overall to hydrolysis of a tertiary amine to form a secondary amine and a primary alcohol. The structure of bpa($VOCl_2$) was established by X-ray diffraction while 2-((*N*,*N*-bis-(2-picolyl)amino)methyl)-6-hydroxymethyl-4-tertbutylphenol was detected by ESI mass spectrometry. The phenol oxygen atom in bpbp($VOCl_2$)(VCl_2) is proposed to be non-bridging and this asymmetry is likely to be important for the C–N bond cleavage reaction. A related asymmetrical V^{IV} complex, [bpbpH(V=O)(H_2O)](ClO_4)$_2$ · H_2O, containing bpbp$^-$ bound to only one metal ion, has also been characterized by X-ray diffraction. In slightly more basic solution, bpbp($VOCl_2$)(VCl_2) is oxidized to the V^{IV}–V^{IV} complex [bpbp$(VOCl)_2$]$^+$ and C–N bond cleavage is suppressed.

Keywords: C–N bond cleavage; Vanadium; Mass spectrometry; X-ray diffraction

1. Introduction

Coordination of organic molecules to transition-metal ions can lead to activation of the former towards reactivity that is unknown or difficult in the absence of the metal. This is the basis of catalysis by metalloenzymes and many industrial catalysts. This manuscript describes N-dealkylation of a tertiary amine group of a phenolate-hinged dinucleating ligand 2,6-bis[bis-(2-pyridylmethyl)aminomethyl]-4-tertbutylphenol (bpbpH; Scheme 1) in the presence of vanadium. Although such processes are often described as oxidative N-dealkylations, the reaction we report amounts to the hydrolysis:

$$R_3N + H_2O \rightarrow R_2NH + ROH$$

N-dealkylation of coordinated amine ligands has been reported previously in the presence of more robust cobalt(III) complexes. Reaction of Co(acac)$_3$ with 1,4,8,11-tetraazabicyclo[9.3.3]heptadecane-5,7-dione (H_2dc3), for example, results in cleavage of the C–N bond in H_2dc3 and formation of a complex of dioxocyclam (dc), Co(dc)(acac) [1]. Several similar examples involving N-dealkylation of Co-coordinated aliphatic amine ligands are also known [2–4]. The most closely related example to that reported here is probably the cleavage and subsequent carboxylation of 2,6-bis(bis(2-pyridylmethyl)amino)methylpyridine in the presence of $Co(ClO_4)_2 \cdot 6H_2O$ to give the carboxylated tris(2-pyridylmethyl)amine complex [Co(tpaCO_2)Cl](ClO_4) [5]. Biomimetic oxidative N-dealkylation of *N*,*N*-dibenzylethylenediamine in the presence of an iron complex and dioxygen has also been reported recently [6]. We are not aware of any analogous reactions in the presence of vanadium.

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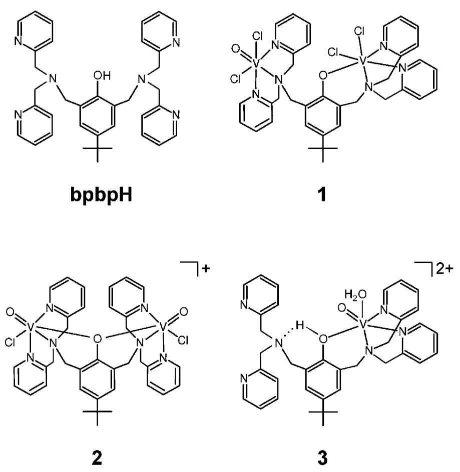

Scheme 1. bpbpH; **1** – bpbp($VOCl_2$)(VCl_2); **2** – [bpbp($VOCl$)$_2$]$^+$; **3** – [bpbpH(V=O)(H_2O)]$^{2+}$.

2. Experimental

2.1. Synthesis

2,6-Bis[bis-(2-pyridylmethyl)aminomethyl]-4-tertbutylphenol (bpbpH) and *N*-methyl-*N*-bis-(2-pyridylmethyl)amine were prepared as described previously [7,8]. All other chemicals were used as supplied from commercial sources. Although we have experienced no difficulties, perchlorate salts of metal complexes are potentially explosive and should be handled with caution.

*2.1.1. 2,6-Bis((N,N-bis-(2-picolyl)amino)methyl)-4-tertbutylphenolate- dichlorovanadium-dichlorovanadyl, bpbp-(VOCl$_2$)(VCl$_2$) (**1**)*

VCl_3 (94.4 mg, 0.600 mmol) and bpbpH (171.0 mg, 0.299 mmol) were mixed in acetonitrile (10 ml). After 10 min at 60 °C complex **1** began to precipitate as a lime-green powder. After 2 h heating, the product was collected, washed with acetonitrile and dried. Yield: 109.7 mg, 44.1%. *Anal.* Calc. for $C_{36}H_{39}N_6O_2Cl_4V_2$: C, 52.00; H, 4.73; N, 10.11; Cl, 17.05. Found: C, 51.75; H, 4.70; N, 10.11; Cl, 16.50%. IR: $\nu_{V=O}$, 973 cm^{-1}.

*2.1.2. 2,6-Bis((N,N-bis-(2-picolyl)amino)methyl)-4-tertbutylphenol-aquovanadyl-bisperchlorate, [bpbpH(V=O)(H$_2$O)](ClO$_4$)$_2$ · H$_2$O (**3** · (ClO$_4$)$_2$ · H$_2$O)*

$VO(ClO_4)_2$ (aq) (3 ml, 0.220 mmol), prepared from $VOSO_4 \cdot 5H_2O$, $BaCO_3$ and conc. $HClO_4$ as described by Wüthrich and Connick [9], was mixed with Hbpbp (90 mg, 0.156 mmol) in methanol (6 ml), water (1 ml) and aqueous 0.01M $HClO_4$ (1 ml). The solution turned brown and crystals of **3** · $(ClO_4)_2 \cdot H_2O$ deposited over 4 days. Yield 66 mg, 47%. ESIMS (methanol) *m/z*: 319.8 ([bpbpH(V=O)]$^{2+}$, 100%), 328.9 ([bpbpH(V=O)-(H_2O)]$^{2+}$, 65%), 335.9 ([bpbpH(V=O)(CH_3OH)]$^{2+}$, 75%), 738.4 ({[bpbpH(V=O)]ClO_4}$^+$, 92%), 756.6 ([bpbpH(V=O)(H_2O)]ClO_4}$^+$, 7%), 770.6 ({[bpbpH(V=O)(CH_3OH)]ClO_4}$^+$, 70%).

*2.1.3. Bis-(2-pyridylmethyl)amine-dichloro-oxo-vanadium, bpa(VOCl$_2$) · CH$_3$CN (**4** · CH$_3$CN)*

The reaction mixture for preparation of **1** was allowed to stand in air for 24 h and **4** · CH_3CN was deposited as turquoise crystals in 15% yield (on the basis of bpbpH). Direct reaction of VCl_3 and bpa in acetonitrile resulted in rapid precipitation of a solid product unsuitable for X-ray analysis.

*2.1.4. Bis-(2-pyridylmethyl)amine-dichloro-oxo-vanadium, bpa(VOCl$_2$) · CH$_3$OH (**4** · CH$_3$OH)*

A solution of bpa (142 mg, 0.715 mmol) in 5 ml of methanol was added dropwise over 3 h to a solution of VCl_3 (98.5 mg, 0.625 mmol) dissolved in 15 ml of methanol. Turquoise crystals of **4** · CH_3OH precipitated overnight. Yield: 83 mg, 36.0%. The crystals decompose on standing and the analysis fit is without methanol. *Anal.* Calc. for $C_{12}H_{13}N_3OCl_2V$: C, 42.76; H, 3.89; N, 12.47. Found: C, 42.87; H, 3.73; N, 12.36%. IR: $\nu_{V=O}$, 958 cm^{-1}.

2.2. Characterization methods

Elemental analyses were performed at the Chemistry Department II, University of Copenhagen, Denmark and at Atlantic Microlab, Inc., Norcross, Georgia 30091, USA. IR spectra of the complexes in KBr discs were measured using a Hitachi 27030 IR spectrometer. Electrospray ionization mass spectra (ESIMS) were obtained using a Finnigan TSQ 700 triple quadrapole instrument equipped with a Finnigan API source in the nanoelectrospray mode.

2.3. Single-crystal X-ray diffraction

Data were collected for **3** · $(ClO_4)_2 \cdot H_2O$ and **4** · CH_3OH at 180(2) K on a Bruker-Nonius X8-APEXII diffractometer, and for **4** · CH_3CN at 150(2) K on a Siemens SMART diffractometer (University of Aarhus, Denmark). Structures were solved and refined using the SHELXTL package [10]. For **3** · $(ClO_4)_2 \cdot H_2O$, the combination of relatively small crystals, a relatively large unit cell ($Z' = 2$) and disordered perchlorate moieties resulted in weak diffraction. The data were truncated to a resolution of 0.95 Å, with approximately 50% observed ($I > 2\sigma I$)) to this resolution. As a result, the structure is of relatively low precision. The high *R* values are attributable in part to inadequate modelling of one grossly disordered perchlorate cation; application of a continuous solvent area model [11] to the structure with this moiety omitted gives $R1 = 0.096$, $wR2 = 0.260$,