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Synthesis and characterization of a *N*-salicylaldimine ligand and its vanadium(V) complex

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ABSTRACT

The reduction of 2-nitro-1,3-di(pyridin-2-yl)-1,3-di(*tert* -butyldimethylsilyloxy)propane **1** with sodium borohydride affords 2-amino-1,3-di(pyridin-2-yl)-1,3-di(*tert*-butyldimethylsilyloxy)propane **2** which was subsequently reacted with salicyl aldehyde yielding *rac*-((2,2,3,3,9,9,10,10-octamethyl-5,7-di(pyridin-2-yl)-4,8-dioxa-3,9-disilaundecan-6-ylimino)methyl)phenol (Proligand **3** = HL($SiMe_2tBu$)$_2$), with excellent yield. Reaction of **3** with vanadyl acetylacetonate followed by aerial oxidation diastereoselectively led to the octahedral coordinated vanadium(V) complex **4**([VO(OMe)L($SiMe_2t$ Bu)]). Compound **3** together with vanadyl acetylacetonate as well as with molybdenyl acetylacetonate shows catalytic activity in the sulfoxidation of (methylsulfanyl)benzene **I**, which was followed by NMR spectroscopy. The vanadium complex **4** was also able to catalyze the sulfoxidation but was considerably slower. All three tested catalytic systems lead to almost quantitative formation of the sulfoxide with only minor formation of the respective sulfone.

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1. Introduction

Since the discovery of vanadium dependent enzymes especially the practical applications of bromo- and chloroperoxidases for the halogenation of organic substrates have triggered research efforts [1,2]. Structural investigations revealed similarities between several phosphatases and the haloperoxidases [3,4]. The active site contains vanadate covalently bound by histidine and stabilized by an H-bonding network with vanadium in a trigonal bipyramidal coordination sphere [5–7]. Vanadium-dependent haloperoxidases were also found to catalyze the oxidation of sulfides to the medically and synthetically important sulfoxides [8]. Thus a wide range of vanadium catalyst, mimicking this enzyme function, were developed. Particularly the development of efficient catalysts for the asymmetric oxidation of sulfides is of interest [8–13]. Among the applied ligands for vanadium complexation, the salicylaldimine moiety was found to be suitable and found widespread application [14–18]. Furthermore, vanadium(IV and V) compounds are not only of interest as catalyst but exhibit insulin-like effects. Particularly coordination compounds were found to be superior over the inorganic salts sodium vanadate or vanadyl sulfate and are in the focus of research [19].

We developed a diastereoselective pathway for the modular preparation of trialkylsilyl protected (*R*,*R*)- and (*S*,*S*)-dipyridylnitrodiols. Conversion of the nitro group offers synthetically valuable functional groups such as amines, oximes or ketones. Particularly the reduction to an amine offers the possibility for Schiff-base formation in order to obtain binding sites for metal ions. In this paper, we like to report on the synthesis and characterization of a new Schiff-base ligand and its vanadium(V) complex starting from the trialkylsilyl protected nitrodiol **1**. The applicability of the new complex as functional mimic for vanadium-dependent haloperoxidase is shown by its catalytic activity towards the sulfoxidation of (methylsulfanyl)benzene **I**. Furthermore, in situ formation of the catalyst and sulfoxidation was also tested with molybdenum(VI).

2. Experimental

2.1. General remarks

All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 200 MHz and Avance 400 MHz spectrometer. Assignment of NMR data was made on the basis of ^{1}H, ^{13}C, DEPT135, HSQC, HMBC, H,H COSY, NOESY and selective NOE experiments. Mass spectra were obtained on a Finnigan MAT SSQ 710 and Finnigan MAZ95XL

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system. Peaks in the mass spectra were assigned by comparison of the observed isotopic patterns with the calculated ones. IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows or neat between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. Absorption spectra were recorded on Perkin-Elmer UV–vis Lambda 16 spectrometer in a 10 mm quartz cuvette at room temperature.

The synthesis of the starting compound **1** was previously described by our group.

*2.1.1. rac-2-Amino-1,3-di(pyridin-2-yl)-1,3-di(tert-butyldimethylsilyloxy) propane (**2**)*

Nickel boride (1.0 g) was suspended in 40 ml of anhydrous methanol and kept for 5 min in an ultrasound bath. To the black suspension a solution of **1** (2.80 g, 5.6 mmol) in 10 ml of anhydrous methanol was added. The mixture was warmed to 40 °C and sodium borohydride (ca. 2.8 g, 74 mmol) was carefully added keeping the internal temperature at 65 °C until TLC (silica, diethylether) indicated the total consumption of **1** (ca. 30 min). The mixture was allowed to cool to room temperature and was carefully filtered over celite (2 cm height). After removal of the solvent in vacuo the residue was stirred in 20 ml of pentane for 15 min. To this mixture 10 ml of water were added and additionally stirred for 10 min. Now the phases were separated and the organic phase was dried over sodium sulfate. After removal of pentane in vacuo 2.39 g of an colorless oil were received. The product still contained traces of the catalyst and was used in the next step without further purifications. The oily product **2** was stable under atmospheric conditions at room temperature. Yield: 90%. Mp 180 °C (9×10^{-3} mbar) dec. ^{1}H NMR ($CDCl_3$): δ = 8.50 (m, 2H, Pyr1, Pyr13), 7.62–7.54 (m, 2H, Pyr3,Pyr11), 7.44 (d, J = 7.8 Hz, 1H, Pyr10), 7.38 (d, J = 8.0 Hz, 1H, Pyr4), 7.12–7.06 (m, 2H, Pyr2, Pyr12), 5.10 (d, J = 5.2 Hz, 1H, H8), 4.72 (d, J = 5.6 Hz, 1H, H6), 3.44 (m, 1H, H7), 0.86 (s, 9H, *tert*-butyl), 0.85 (s, 9H, *tert*-butyl), 0.30 (s, 3H, $SiCH_3$), −0.04 (s, 3H, $SiCH_3$), −0.28 (s, 3H, $SiCH_3$), −0.35 (s, 3H, $SiCH_3$), 1.50 (s broad, 2H, NH). ^{13}C NMR ($CDCl_3$): δ = 148.8 and 148.3 (t, Pyr1, Pyr13), 135.9 (t, Pyr11), 135.6 (t, Pyr3), 122.6 (t, Pyr10), 122.4 (t, Pyr4), 122.0 (t, Pyr2, Pyr12), 162.6 (q, Pyr9), 162.1 (q, Pyr5), 75.4 (t, C8), 76.9 (t, C6), 62.8 (t, C7), 25.9 (p, *tert*-butyl), 25.6 (p, *tert*-butyl), 18.2 (q, *tert*-butyl), 18.1 (q, *tert*-butyl), −3.6 (p, $SiCH_3$), −4.5 (p, $SiCH_3$), −4.7 (p, $SiCH_3$), −4.9 (p, $SiCH_3$). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3391 st, broad (NH), 3067 m, 3012 m, 2928 st, 2894 st, 2856 st, 2739 w, 2710 w, 1650 m, 1591 st (C=N), 1572 st (C=C), 1471 st, 1435 st, 1407 st, 1389 st, 1254 st, 1216 m, 1075 st, 1005 st, 938 st, 837 st, 777 st, 673 st, 619 m, 597 st, 575 m, 535 m. MS (FAB in nba): m/z (%) = 496 (49) [M+Na]$^+$, 474 (63) [M+1]$^+$, 416 (11) [M-*tert*-butyl]$^+$, 399 (19), 342 (26), 325 (25), 267 (20), 261 (19), 251 (100), 235 (61), 223 (62), 208 (38). $C_{25}H_{43}N_3O_2Si_2$ (473.78).

*2.1.2. rac-((2,2,3,3,9,9,10,10-Octamethyl-5,7-di(pyridin-2-yl)-4,8-dioxa-3,9-disilaundecan-6-ylimino)methyl)phenol (**3**)*

Amino compound **2** (1.50 g, 32 mmol) and salicyl aldehyde (0.39 g, 32 mmol) were solved in 40 ml of methylene chloride and molecular sieve 4A was added. The solution was refluxed for 1 h until TLC (silica, diethyl ether) indicated the total consumption of **2**. Subsequently the solution was filtered over celite and the solvent was removed in vacuo, yielding a yellow viscous oil. The oil was dried in vacuo for several hours affording the solid product **3** with high purity. Yield: 98%. Mp 84 °C. ^{1}H NMR (CD_3OD): δ = 8.38 (s, 1H, HC=N), 8.47 (d, J = 4.4 Hz, 1H, Pyr13), 8.50 (d, J = 4.4 Hz, 1H, Pyr1), 7.75 (ddd, J = 7.6 1.6 Hz, 1H, Pyr11), 7.63–7.59 (m, 1H, Pyr3), 7.31–7.26 (m, 3H, Ph12, Ph16, Ph18), 7.60 (d, J = 7.6 1.6 Hz, 1H, Pyr10), 7.21–7.18 (m, 2H, Pyr2, Pyr4), 6.84 (t, J = 7.6 Hz, 1H, Ph17), 6.80 (d, J = 8.0 Hz, 1H, Ph19), 4.07 (dd, J = 8.0 Hz, J = 2.8 Hz, 1H, H7), 4.88 (d, J = 2.8 Hz, 1H, H6), 5.26 (d, J = 8.0 Hz, 1H, H8), 0.87 (s, 9H, *tert*-butyl), 0.64 (s, 9H, *tert*-butyl), −0.12 (s, 3H, $SiCH_3$), −0.20 (s, 3H, $SiCH_3$), −0.28 (s, 3H, $SiCH_3$), −0.32 (s, 3H, $SiCH_3$), 12.7 (s broad, H, OH in $CDCl_3$). ^{13}C NMR (CD_3OD): δ = 168.9 (t, HC=N), 162.7 (q, Pyr5), 162.2 (q, Pyr9), 150.0 (t, Pyr13), 149.1 (t, Pyr1), 138.1 (t, Pyr11), 137.7 (t, Pyr3), 133.7 and 132.9 (t, Ph16,Ph18), 124.5 (t, Pyr12), 125.9 (t, Pyr10), 123.6 and 123.5 (t, Pyr2, Pyr4), 120.1 (q, Ph15), 119.6 (t, Ph17), 117.8 (t, Ph19), 82.1 (t, C7), 76.5 (t, C6), 75.8 (t, C8), 26.3 (t, *tert*-butyl), 26.2 (t, *tert*-butyl), 19.0 (q, *tert*-butyl), 18.8 (q, *tert*-butyl), −4.6 (p, $SiCH_3$), −4.65 (p, $SiCH_3$), −4.7 (p, $SiCH_3$), −4.8 (p, $SiCH_3$). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 3100–2900 m (OH), 3073 w, 2728 w, 2668 w, 1633 st (C=N exocyc.), 1615 m, 1587 st (C=N endocyc.), 1571 m (C=C), 1500 m, 1316 m, 1282 st, 1251 st, 1212 w, 1149 m, 1110 st, 1075 st, 1044 w, 1005 m, 988 m, 966 m, 939 w, 891 m, 845 st, 837 st, 776 st, 761 m, 750 st, 738 w, 669 w, 641 w, 624 w, 609 w, 577 w, 545 w. MS (DEI): m/z (%) = 577 (32) [M]$^+$, 562 (6), 520 (41) [M-*tert*-butyl]$^+$, 355 (61), 223 (100), 178 (12), 165 (17), 73 (26), 28 (20). UV–vis (ethanol, lmol^{-1} cm^{-1}): ϵ (λ_{max}) = 1.9×10^4 (257 nm), 4410 (317 nm), 343 (410 nm). $C_{32}H_{47}N_3O_3Si_2$ (577.90): Calc. C, 66.51; H, 8.20; N, 7.27. Found: C, 66.34; H, 8.35; N, 6.98.

*2.1.3. [(2-((1-(tert- Butyldimethylsilyloxy)-3-hydroxo-1,3-di(pyridin-2-yl) propan-2- ylimino)methyl)phenolato)(methanolato)oxidovanadium(V)] (**4**)*

Proligand **3** (200 mg, 0.35 mmol) and vanadyl acetylacetonate (92 mg, 0.35 mmol) were solved in 12 ml of anhydrous methanol under argon atmosphere. The green to yellow mixture was refluxed for 4 h and stirred over night at room temperature. Subsequently, a solution of potassium hydroxide (20 mg, 35 mmol) in 5 ml of methanol was added and the mixture was vigorously stirred over night at room temperature in an open vessel. Upon aerial oxidation the solution slowly colored red. Thereafter, the red solution was filtered and left for crystallization. Crystals suitable for single crystal X-ray diffraction were obtained by slow solvent evaporation. The crystallized complex **4** was found to be stable under atmospheric conditions at room temperature. Yield: 70%. Mp 130 °C (dec.). ^{1}H NMR (CD_3OD): δ = 6.90 (s, 1H, HC=N), 8.58 (d, J = 4.4 Hz, 1H, Pyr13), 8.26 (d, J = 4.8 Hz, 1H, Pyr1), 7.83 (ddd, J = 7.6 Hz, J = 1.2 Hz, 1H, Pyr3), 7.76 (ddd, J = 7.6, J = 1.6 Hz, 1H, Pyr11), 7.42–7.35 (m, 3H, Pyr12, Pyr10, Ph18), 6.57 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H, Ph16), 7.27–7.24 (m, 1H, Pyr2), 7.52 (d, J = 8.0 Hz, 1H, Pyr4), 6.64 (t, J = 7.2 Hz, 1H, Ph17), 6.86 (d, J = 8.4 Hz, 1H, Ph19), 6.08 (s broad, 1H, H6), 5.11 (s, OCH_3), 4.04 (d, J = 8.8 Hz, 1H, H7), 5.68 (d, J = 8.8 Hz, 1H, H8), 0.96 (s, 9H, *tert*-butyl), 0.25 (s, 3H, $SiCH_3$), −0.04 (s, 3H, $SiCH_3$). ^{13}C NMR (CD_3OD): δ = 166.7 (t, HC=N), 162.5 (q, Pyr5), 161.0 (q, Pyr9), 150.4 (t, Pyr13), 148.3 (t, Pyr1), 139.7 (t, Pyr3), 138.6 (t, Pyr11), 136.7 (t, Ph18), 165.5 (q, Ph20), 133.6 (t, Ph16), 125.9 (t, Pyr12), 125.1 (t, Pyr10), 124.6 (t, Pyr2), 121.8 (q, Ph15), 120.9 (t, Pyr4), 119.7 (t, Ph17), 119.1 (t, Ph19), 87.3 (t, C6), 85.7 (t, C7), 77.6 (t, C8), 73.5 (p, OCH_3), 26.3 (p, *tert*-butyl), 19.2 (q, *tert*-butyl), 3 (−4.7, $SiCH_3$), −4.4 (p, $SiCH_3$). ^{51}V NMR ($CDCl_3$): δ = −518. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 2725 w, 1636 st (C=N exocyc), 1599 st (C=N endocyc), 1587 m (C=N endocyc), 1568 m (C=C), 1552 m (C=C), 1420 m, 1338 m, 1323 m, 1297 st, 1282 st, 1250 st, 1219 m, 1153 st, 1125 m, 1076 st, 1055 st, 1015 m, 1003 m, 991 m, 971 m, 959 st (V=O), p 939 (m), 890 m, 862 st, 846 st, 813 m, 797 m, 777 m, 764 st, 743 st, 722 m, 670 w, 646 w, 639 w, 624 st, 607 st, 596 st, 579 m, 554 m, 534 st, 511 m, 467 m. MS (DEI): m/z (%) = 559 (<1) [M]$^+$, 543 (2) [M−CH_3]$^+$, 527 (40), 502 (55) [M-*tert*-butyl]$^+$, 452 (74), 420 (100), 395 (35), 364 (53), 320 (24), 306 (40), 290 (78), 166 (25), 73 (79), 32 (26). UV–vis (ethanol, lmol^{-1} cm^{-1}): ϵ (λ_{max}) = 3×10^4 (230 nm), 8×10^3 (330 nm), 3×10^3 (460 nm).

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