

2,5-Dimethyl-3,6-bis[(2,6-diisopropylphenylimino)methyl]- and 2,6-Bis[(2,6-diisopropylphenylimino)methyl]pyrazine: Two New Chelating Ligands for Transition Metal Complexes

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The reaction of tetramethylpyrazine with SeO_2 yields 2,5-dimethylpyrazine-3,6-dicarboxaldehyde (**1**) from which the 2,5-dimethyl-3,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine (**2**) was synthesized by treatment with 2 equivalents of 2,6-diisopropylaniline. 2,6-Dimethylpyrazine reacts with benzaldehyde to give 2,6-distyrylpyrazine (**3**). Ozonolysis of **3**, followed by treatment with Na_2SO_3 and 2,6-diisopropylaniline resulted in the formation of 2,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine (**5**) together with [(2,6-diisopropylphenylimino)methyl]benzene (**6**).

Key words: Diimine, Dialdehyde, Pyrazine, Chelating Ligands

Introduction

Nitrogen containing organic compounds, in particular pyridine and/or imine derivatives, are very important ligands widely used in various organometallic complexes for olefin oligomerization and polymerization [1]. In general, the performance of the catalysts is regulated by the structure of the ligands. Therefore the synthesis of new ligands is one of the keys for the development of new catalysts.

Usually, imine containing ligands are prepared *via* condensation of carbonyl compounds with aniline derivatives bearing bulky substituents [1]. Because of the smoothly proceeding condensation of the carbonyl group with aniline under mild conditions [2], the key to the preparation of such ligands is the synthesis of starting materials containing suitable carbonyl groups.

Widely used methods to prepare aldehydes are the oxidation of α -methyl groups or of unsaturated compounds by SeO_2 [3], O_3 [4], and other oxidants [5]. In this paper we describe the synthesis of two new chelating ligand systems derived from 2,5-dimethylpyrazine-3,6-dicarboxaldehyde and pyrazine-3,6-dicarboxaldehyde.

Results and Discussion

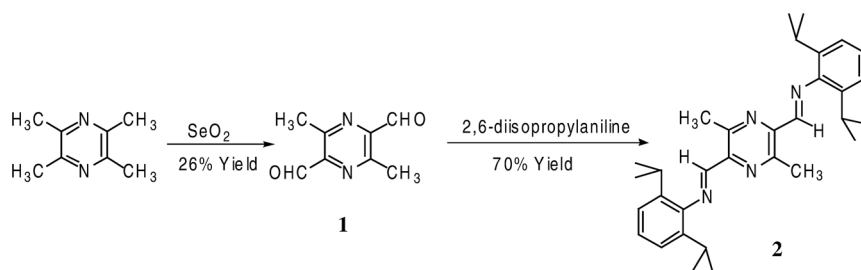
The reaction of 2,3,5,6-tetramethylpyrazine with a tenfold amount of SeO_2 in wet dioxane results

in the formation of 2,5-dimethylpyrazine-3,6-dicarboxaldehyde (**1**) in 26% yield as a yellow powder. This product reacts with 2 equivalents of 2,6-diisopropylaniline yielding yellow 2,5-dimethyl-3,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine (**2**) in 70% yield (Scheme 1).

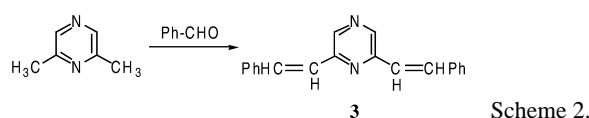
First attempts to prepare 2,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine in analogy to **2** *via* SeO_2 oxidation of 2,6-dimethylpyrazine failed. The reaction temperature of more than 100 °C does not allow the isolation of pyrazine-2,6-dicarboxaldehyde, which decomposes quickly after generation. Therefore we chose another route which can be used for the synthesis of thermally and oxidatively labile aldehydes, *vic.* the oxidation of olefins with ozone, the reduction of the resulting ozonides with Na_2SO_3 , followed by condensation with 2,6-diisopropylaniline [4].

Using a modification of the method successfully employed for the synthesis of 2,5-distyrylpyrazine [4b, 6], 2,6-distyrylpyrazine (**3**) was prepared in high yield by condensation of 2,6-dimethylpyrazine with benzaldehyde (Scheme 2).

Treatment of **3** with ozone at -50 °C, followed by reduction of the ozonide formed with Na_2SO_3 in methanol at -50 °C and condensation of the dialdehyde **4** with 2,6-diisopropylaniline at room temperature resulted in 2,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine (**5**), and [(2,6-diisopropylphen-



Scheme 1.



Scheme 2.

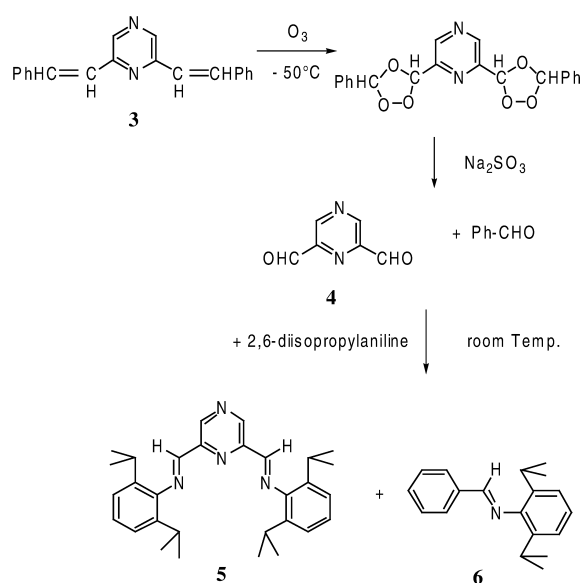
ylimino)methyl]benzene (**6**) which were separated by column chromatography (Scheme 3). The dioxonide as well as the dialdehyde **4** were not isolated and characterized, but used in the “one-pot” reaction without further purification.

In conclusion, two new poly-*N*-functional Schiff-base ligands were synthesized *via* the dialdehydes. Each of them has two imine groups and two nitrogen atoms in the aromatic pyrazine system. Obviously, both are very good potential ligands, of which **2** can be used as a bis-chelating ligand which can coordinate with two metal centers, and **5** as a tridentate ligand and to prepare various transition metal complexes for catalysis.

Experimental Section

All operations were carried out in an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried over sodium, purified and saturated with nitrogen prior to use. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Mass spectra (EI, 70 eV) were obtained using a Varian MAT 311A instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 200 (200 and 50.32 MHz, respectively) and a Bruker ARX 400 (400 and 100.64 MHz, respectively) spectrometer in CDCl_3 unless otherwise stated.

2,5-Dimethylpyrazine-3,6-dicarboxaldehyde (1): Tetramethylpyrazine (1.9 g, 14 mmol) and SeO_2 (15.4 g, 140 mmol) were dissolved in a mixture of dioxane (240 ml) and water (10 ml) and refluxed for 5 h. After filtration of the black powder received, the clear filtrate was concentrated nearly to dryness. Toluene (120 ml) was added, the mixture was refluxed for 30 min, decanted from the remaining residue and the solvents were evaporated to leave a volume of 10 ml. Yellow needles of **1** separated and were collected by filtra-



Scheme 3.

tion. Yield: 0,60 g (26%). M. p. 140–142 °C. – ^1H NMR (200 MHz): δ = 2.86 (s, 6 H, CH_3), 10.16 (s, 2 H, CHO). – ^{13}C NMR (50.32 MHz): δ = 21.36 (CH_3), 144.65 (CCH_3), 151.95 (CCHO), 193.56 (CCHO).

2,5-Dimethyl-3,6-bis[(2,6-diisopropylphenylimino)methyl]pyrazine (2): A mixture of **1** (0,58 g, 3.5 mmol), 2,6-diisopropylaniline (1,4 ml) and acetic acid (0,1 ml) in ethanol (8 ml) was refluxed for 15 h with stirring. Filtration of the reaction mixture at room temperature and washing of the resulting yellow powder with ethanol (5 ml) yielded **2** (1.19 g, 70%). M. p. 220–222 °C. – ^1H NMR (200 MHz): δ = 1.26 [d, 3J = 6.9 Hz, 24 H, $\text{CH}(\text{CH}_3)_2$], 3.08 [sept, 3J = 6.9 Hz, 4 H, $\text{CH}(\text{CH}_3)_2$], 3.11 [s, 6 H, CH_3 (pyr)], 7.21–7.27 (m, 6 H, Ph), 8.57 (s, 2 H, $\text{CH}=\text{N}$). – ^{13}C NMR (50.32 MHz): δ = 23.24 [CH_3 (py)], 23.45 (CHCH_3), 28.02 (CHCH_3), 123.01 (Ph), 124.63 (Ph), 136.72 (Ph), 145.32 (C-pyr), 149.02 (Ph), 151.24 (C-pyr), 163.53 ($\text{CH}=\text{N}$). – $\text{C}_{32}\text{H}_{42}\text{N}_4$ (482.71): calcd. C 79.62, H 8.77, N 11.61; found C 79.68, H 8.53, N 11.78.

2,6-Distyrylpyrazine (3): A mixture of 2,6-dimethylpyrazine (2.1 g, 20 mmol), ZnCl_2 (2.8 g, 20 mmol) and benzalde-

hyde (30 ml) was heated to 155 °C for 8 h with stirring. Then ethanol (30 ml) was added, the reaction mixture refluxed for 30 min and cooled to room temperature and filtered. The remaining yellow powder was washed with ethanol (20 ml) and dried in vacuum yielding 5.45 g (100%) of **3**. M.p. 229–230 °C.

2,6-Bis[(2,6-diisopropylphenylimino)methyl]pyrazine (5) and [(2,6-Diisopropylphenylimino)methyl]benzene (6): A solution of **3** (2.1 g, 20 mmol) in methanol (200 ml) was cooled in a CO₂/isopropanol bath to –50 °C and O₃ was bubbled through the stirred solution until complete dissolution of **3** and appearance of the pale blue colour of dissolved O₃ (6–8 h). Excess of O₃ was then displaced by bubbling N₂ through the solution until the pale blue colour disappeared. Finely ground Na₂SO₃ (8.25 g) was added and the solution was stirred for 5 h at –50 °C. The reaction mixture was warmed to room temperature and a white solid was filtered off. 2,6-Diisopropylaniline (6.2 ml) and acetic acid (0.3 ml) were added to the remaining clear solution, which was then stirred for one week at room temperature. Evaporation of methanol under vacuum left a few ml of a yellow solution, from which 0.5 g (16%) of **5** and 0.45 g (12%) of **6** were isolated by column chromatography (toluene).

5: M.p. 133–134 °C. – ¹H NMR (400 MHz): δ = 1.26 (d, ³J = 6.9 Hz, 24 H, CH₃), 3.04 [sept, ³J = 6.9 Hz, 4 H, CH(CH₃)₂], 7.21–7.27 (m, 6 H, Ph), 8.47 (s, 2 H, CH=N), 9.65 [s, 2 H, H(pyr)]. – ¹³C NMR (100.64 MHz): δ = 23.39 (CH₃), 27.98 (CHCH₃), 123.17 (Ph), 124.99 (Ph), 137.03 (Ph), 144.25 (C-pyr), 147.94 (Ph), 148.49 (C-pyr), 160.97 (CH=N). – C₃₀H₃₈N₄ (445.66): calcd. C 79.25, H 8.42, N 12.32; found C 79.09, H 8.58, N 12.31.

6: M.p. 123–124 °C. – ¹H-NMR (400 MHz): δ = 1.24 (d, ³J = 6.8 Hz, 12 H, CH₃), 3.06 [sept, ³J = 6.8 Hz, 2 H, CH(CH₃)₂], 7.18–7.24 (m, 3 H, Ph_{m,p}), 7.98–8.00 (m, 2 H, Ph_o), 8.27 (s, 1 H, CH=N). – ¹³C NMR (100.64 MHz): δ = 23.42 (CH₃), 27.86 (CHCH₃), 123.02 (C₆H₃-3,5), 124.13 (C₆H₃-4), 128.59 (C₆H₅-3,5), 128.83 (C₆H₅-2,6), 131.44 (C₆H₅-4), 136.01 (C₆H₅-1), 137.60 (C₆H₃-2,6), 149.24 (C₆H₃-1), 162.03 (CH=N).

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