Supporting Information

Oxidation-Reductive Coupling of Alcohols Catalyzed by Oxo-Vanadium Complexes

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Preparation of Ligands and Vanadium Complexes

NBu₄VO₃ was prepared as described by Day et al. (V.W. Day, W.G. Klemperer and A. Yagasaki, Chem. Lett. 1990, 1267).

Preparation of Salicylimine ligand

Salicaldehyde (1.77 g, 14.5 mmol) was dissolved in methanol (200 mL). 2-Aminophenol (1.58 g, 14.5 mmol) is then added. The solution was heated at reflux for 2 h. After cooling to rt for 1-2 days a dark orange-red crystalline solid formed and was collected by filtration and air dried. NMR: (300 MHz, DMSO-d₆) δ 13.84 (s, 1H), 9.79 (s, 1H), 8.99 (s, 1H), 7.64 (dd, 1H, J = 8.0, 1.7 Hz), 7.46-7.36 (m, 2H), 7.16 (ddd, 1H, J = 8.0, 7.4, 1.6 Hz), 7.03-6.95 (m, 3H), 6.91 (ddd, 1H, J = 8.6, 7.6, 1.4 Hz).

Preparation of S₂-dipic ligand


Preparation of 2

Pyridine 2,6-dithiocarboxylic acid (0.053 g, 0.267 mmol) is dissolved in acetone (50 mL) followed by the addition of Bu₄NVO₃ (0.091 g, 0.266 mmol). The solution turned brown immediately and darkened while stirring overnight. The solvent is removed in vacuo, leaving Bu₄N(S₂-dipic)VO₂ (0.151 g) as a light brown, polycrystalline solid, which was spectroscopically pure and used without further purification in the reactivity study.

IR (KBr pellet, cm⁻¹): 3087 (m, νC-H), 2962, 2983 (s, νC-H), 1675 (s, νO=O), 1491 (m, νC=O), 1342 (w, νC=C), 949 (m, νV=O), 751 (m, νV-O).

¹H NMR (CDCl₃, ppm, 400 MHz): 8.35 (broad, para), 8.20 (broad, meta), 3.41 (broad, NCH₂CH₂CH₂CH₃), 1.73 (broad, NCH₂CH₂CH₂CH₃), 1.46 (broad, NCH₂CH₂CH₂CH₃), 0.98 (broad, NCH₂CH₂CH₂CH₃).

¹³C{¹H} NMR (CDCl₃, ppm, 400 MHz): 167.44 (s, O=C-O), 149.74 (s, ortho to N), 144.86 (s, para to N), 125.48 (s, meta to N), 58.74 (s, NCH₂CH₂CH₂CH₃), 23.96 (s, NCH₂CH₂CH₂CH₃), 19.70 (s, NCH₂CH₂CH₂CH₃), 13.66 (s, NCH₂CH₂CH₂CH₃).

Preparation of 3

Method 1: NBu₄VO₃ (0.186 g, 0.545 mmol) is dissolved in methanol (50 mL). Then the ligand 1 (0.113 g, 0.545 mmol) was added. The color changed immediately to a dark brown color and the solution was stirred overnight. The solvent was removed under vacuum, leaving dark brown complex 3 (0.295 g) as an amorphous solid, which was spectroscopically pure and used as is in the reactivity study.
Method 2: NBut$_4$VO$_3$ (0.305 g, 0.892 mmol) is dissolved in dry THF (50 mL). Then compound 1 (0.190 g, 0.892 mmol) was added. The color changed immediately to a dark brown color, and the solution was stirred overnight. The solvent was removed under vacuum, leaving catalyst 3 (0.460 g), which was spectroscopically pure.

**IR (KBr pellet, cm$^{-1}$):** 3094 (m, $\nu$C-H), 2971 (s, $\nu$C-H), 2876 (s, $\nu$C-H), 1609 (s, $\nu$N=C), 1532 (m, $\nu$C=C), 1472 (m, $\nu$C=C), 1291 (m, $\nu$N-C), 981 (s, $\nu$V=O), 752 (m, $\nu$V=O).

**$^1$H NMR (CDCl$_3$, ppm, 400 MHz):** 9.01 (H1), 7.53 (H9), 7.45 (H6), 7.33 (H4), 7.08 (H11), 7.00 (H12), 6.81 (H5/H3), 6.69 (H10), 3.45 (H14), 1.64 (H15), 1.35 (H16), 0.93 (H17).

**$^{13}$C{$^1$H} NMR (CDCl$_3$, ppm, 400 MHz):** 167.11 (s, C7), 164.38 (s, C13), 154.22 (s, C1), 136.88 (s, C2), 133.47 (s, C4), 133.07 (s, C6), 128.56 (s, C11), 121.58 (s, C8), 120.69 (s, C5), 119.84 (s, C12), 117.14 (s, C10), 116.28 (s, C3), 113.86 (s, C9), 58.20 (s, C14), 23.86 (s, C15), 19.61 (s, C16), 13.68 (s, C17).

Preparation of 4

From 3 recrystallized in MeOH: Compound 3 (0.150 g, 0.279 mmol) is dissolved in 25 mL MeOH. The flask was sealed to slow the evaporation. Over the next 2 weeks, crystals began to form on the side of the flask. The solution is then removed, leaving compound 4, a brown, crystalline solid. The structure of 3, as a methanol adduct was verified by X-ray diffraction. The NMR and IR data for 3 were in agreement with those reported (Kraehmer, V.; Rehder, D. Dalton Transactions 2012, 41, 5225-5234).

**From OV(O^t^Pr)$_3$ + LH$_2$ in MeOH:** OV(O^t^Pr)$_3$ (0.590 g, 2.42 mmol) is dissolved in MeOH (100 mL). To this solution, the imine ligand LH$_2$ (0.515 g, 2.42 mmol) is added. After stirring overnight, the solvent is removed under vacuum, leaving 4 (0.801 g, 2.37 mmol, 98 %), a dark brown polycrystalline solid, which was spectroscopically pure and used as is in the reactivity study.

**IR (KBr pellet, cm$^{-1}$):** 3096 (w, $\nu$C-H), 2942 (w, $\nu$C-H), 1605 (s, $\nu$N=C), 1537 (m, $\nu$C=C), 1451 (m, $\nu$N-C), 1295 (m, $\nu$C=C), 982 (s, $\nu$V=O).

**$^1$H NMR (CDCl$_3$, ppm, 400 MHz):** 9.17 (s, H1), 7.70 (d, H6, $^3$J(H-1-H) = 7.8 Hz), 7.63 (t, H4, $^3$J(H-1-H) = 7.9 Hz), 7.61 (d, H9, $^2$J(H-1-H) = 7.9 Hz), 7.30 (t, H11, $^3$J(H-1-H) = 8.1 Hz), 7.20 (d, H3, $^3$J(H-1-H) = 8.4 Hz), 7.12 (t, H5, $^3$J(H-1-H) = 7.5 Hz), 7.03 (d, H12, $^3$J(H-1-H) = 8.2 Hz), 6.97 (t, H10, $^3$J(H-1-H) = 7.7 Hz), 5.33 (s, H14).

**$^{13}$C{$^1$H} NMR (CDCl$_3$, ppm, 400 MHz):** 165.64 (s, C7), 164.66 (s, C13), 154.02 (s, C1), 136.38 (s, C2), 135.40 (s, C4), 132.97 (s, C6), 130.18 (s, C11), 121.26 (s, C8), 120.18 (s, C10), 118.37 (s, C3), 116.37 (s, C3), 113.86 (s, C9), 58.20 (s, C14), 23.86 (s, C15), 19.61 (s, C16), 13.68 (s, C17).
Representative Procedure for Oxidation/Reductive Coupling of Alcohols

Into a 10 mL glass pressure tube (Ace Glass) was added the catalyst (0.100 mmol), benzhydrol (0.184 g, 1.00 mmol), 5 mL of benzene and a magnetic spin bar. The tube was purged with nitrogen, manually sealed and then heated with stirring at 150 °C for 24 h. To determine the percent conversion and a yield by NMR, 300 µL of the reaction mixture were dispensed into an NMR tube, along with 5 µL of DMF and ca. 500 µL of CDCl₃. A ¹H NMR spectrum was obtained and processed using MestreNova. The integration of the signals relative to the DMF signals is used to ascertain the amounts for percent conversion and yield.

Procedure for Reductive Coupling Kinetics Experiment

In a pressure tube, the catalyst (0.100 mmol) is added to benzhydrol (0.184 g, 1.00 mmol). Benzene (5 mL) is added and the tube is purged with N₂. The tube is then sealed and heated to 150 °C for 2, 4, 8, 17, or 24 h.

D-Benzhydrol synthesis

In a dry Schlenk flask, NaBD₄ (0.0776 g, 1.85 mmol) is suspended in Et₂O (25 mL) and cooled to 0 °C. Benzophenone (0.309 g, 1.70 mmol) is added to the flask followed by the slowwise addition of MeOH (20 mL). The solution is stirred overnight and 5 mL of H₂O is added. The solvent is removed in vacuo, the crude product is then dissolved in Et₂O, and the solution dried over Na₂SO₄. After filtration to remove the drying agent, the solvent is removed in vacuo, leaving d-benzhydrol (0.111 g, 0.601 mmol, 35.4%). The EI-Mass spectrum was used to confirm that the product was 98.3% d₁-benzhydrol.

Kinetic Isotope Effect

D₁-benzhydrol (0.111 g, 0.60 mmol) and H₂-benzhydrol (0.107 g, 0.60 mmol) are mixed. In a pressure tube, the catalyst 3 (0.0536 g, 0.100 mmol) is added to the benzhydrol mixture. Benzene (5 mL) is added and the tube is purged with nitrogen, then sealed and heated to 150 °C for 24 h. MS analysis on page S32.

Configurational stability of 1-phenylethanol under RC conditions

Complex 3 (0.103 g, 0.191 mmol) is placed in a pressure reactor tube. S-1-phenylethanol (0.252 g, 2.07 mmol) is added along with benzene (5 mL). The tube is sealed and heated for 2 h. The unreacted alcohol substrate is separated using column chromatography over SiO₂ with a 1:1 mixture of ethyl acetate:hexane as the eluent. The solvents were removed in vacuo, leaving the 1-phenylethanol (0.226 g, 1.85 mmol, 89.6% recovered). Measured optical rotations, [(ROH) = 1.2 g/100 mL, CHCl₃]: pure S-1-phenylethanol: - 0.27°; recovered alcohol after reaction: - 0.076°. % ee = 28, 64 % S, 36 % R.
S2-dipic VO2

NBu₄⁺
Ph\_C=O

Benzene (0.1 M)
150 °C, 24 h

Ph\_C=CH\_2 OH + \[
\begin{array}{c}
\text{Ph} \\
\text{H} \\
\text{Ph} \\
\text{H} \\
\end{array}
\]

(10 mol %)
Ph<sub>2</sub>OH + [Structural formula]
Benzene (0.1 M)
150 °C, 24 h

Ph<sub>2</sub>OH + [Structural formula]

Ph<sub>2</sub>CO

Ph<sub>2</sub>CCH<sub>3</sub>
Benzene (0.1 M)
150 °C, 24 h
Benzene (0.1 M)
150 °C, 24 h
Benzene (0.1 M)
150 °C, 24 h
Benzene (0.1 M)
150 °C, 24 h

(10 mol %)

(2 isomers)
C

\[ \text{OH} \]

\[ \text{Ph} \]

D

\[ \text{H}_3\text{C} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{H} \]

\[ \text{CH}_3 \]

(2 isomers)
Computational Methods

The B3LYP \cite{Becke93} method resident in Gaussian 09 \cite{Frisch09} was used to determine the energy minimized structures and electronic energies of Figure 2 (0 K, vacuum); the 6-31-G(d) basis set was used for H, C, N, O atoms and LANL2DZ for V.
