

Supplementary Information for

**New Dioxo–Molybdenum(VI) and –Tungsten(VI) Complexes
with *N*-capped Tripodal N_2O_2 Tetradentate Ligands:
Synthesis, Structures and Catalytic Activities
towards Olefin Epoxidation**

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EXPERIMENTAL

1. Synthesis of mono- and di-*tert*-butyl substituted 2-hydroxybenzaldehydes

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde. To a solution mixture of 3,5-di-*tert*-butylphenol (20.6 g, 100 mmol) and tributylamine (9.6 cm³, 40.0 mmol) in toluene (15 cm³) was added SnCl₄ (1.2 cm³, 10.0 mmol) dropwise under N₂. White fumes appeared immediately during the addition and stirring was continued for 15 min at room temperature. Then paraformaldehyde (6.60 g, 220 mmol) was added in a single portion and the mixture was heated at 100 °C for 10 h. After cooling to room temperature, water (20 cm³) was added and the residue was extracted with Et₂O (6 × 100 cm³). The combined extracts were dried over anhydrous MgSO₄, concentrated and chromatographed using CHCl₃ / hexane (1:1) as eluent. The first band was collected and rotary evaporated to give a pale yellow solid. Yield: 19.2 g (82%). ¹H NMR (CDCl₃): δ 9.87 (s, 1 H, CHO), 7.60 (d, *J* = 2.4 Hz, 1 H, ArH), 7.35 (d, *J* = 2.4 Hz, 1 H, ArH), 1.43 (s, 9 H, ^tBu), 1.33 (s, 9 H, ^tBu).

3-*tert*-Butyl-2-hydroxybenzaldehyde. This compound was synthesised from 3-*tert*-butylphenol (15.0 g, 100 mmol), tributylamine (9.6 cm³, 40.0 mmol), paraformaldehyde (6.60 g, 220 mmol), and SnCl₄ (1.2 cm³, 10.0 mmol) in toluene (15 cm³) using a procedure similar to that for the preparation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. The product was isolated as a pale yellow liquid. Yield: 13.4 g (75%). ¹H NMR (CDCl₃): δ 9.87 (s, 1 H, CHO), 7.53 (dd, *J* = 1.7, 7.7 Hz, 1 H, ArH), 7.39 (dd, *J* = 1.7, 7.7 Hz, 1 H, ArH), 6.94 (t, *J* = 7.7 Hz, 1 H, ArH), 1.42 (s, 9 H, ^tBu).

5-*tert*-Butyl-2-hydroxybenzaldehyde. This compound was synthesised from 5-*tert*-butylphenol (15.0 g, 100 mmol), tributylamine (9.6 cm³, 40.0 mmol), paraformaldehyde (6.60 g, 220 mmol), and SnCl₄ (1.2 cm³, 10.0 mmol) in toluene (15 cm³) using a procedure similar to that for the preparation of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. The product was isolated as a pale brown liquid. Yield: 13.0 g (73%). ¹H NMR (CDCl₃): δ 9.89 (s, 1 H, CHO), 7.59 (dd, *J* = 2.4, 8.7 Hz, 1 H, ArH), 7.52 (d, *J* = 2.4 Hz, 1 H, ArH), 6.94 (d, *J* = 8.7 Hz, 1 H, ArH), 1.33 (s, 9 H, ^tBu).

2. Synthesis of mono- and di-*tert*-butyl substituted 2-hydroxybenzyl alcohols

3,5-Di-*tert*-butyl-2-hydroxybenzyl alcohol. NaBH₄ (1.13 g, 30.0 mmol) was slowly added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.52 g, 15.0 mmol) in MeOH (50 cm³). The reaction mixture turned from pale yellow to colourless during the addition and stirring was continued for 1 h at room temperature. All the volatiles were then removed using a rotary evaporator and the residue was mixed with water (50 cm³). The resulting mixture was neutralised with glacial acetic acid before being extracted with CH₂Cl₂ (3 × 150 cm³). The combined extracts were dried over anhydrous MgSO₄, concentrated to give a white crystalline solid. Yield: 3.44 g (97%). ¹H NMR (CDCl₃): δ 7.53 (bs, 1 H, ArOH), 7.28 (s, 1 H, ArH), 6.90 (s, 1 H, ArH), 4.85 (s, 2 H, ArCH₂), 1.43 (s, 9 H, ^tBu), 1.28 (s, 9 H, ^tBu).

3-*tert*-Butyl-2-hydroxybenzyl alcohol. This compound was synthesised from 3-*tert*-butyl-2-hydroxybenzaldehyde (4.34 g, 24.4 mmol) and NaBH₄ (1.84 g, 48.8 mmol) in MeOH (50 cm³) using a similar procedure as described for 3,5-di-*tert*-butyl-2-hydroxybenzyl alcohol. The product was isolated as a pale yellow liquid. Yield: 4.22 g (96%). ¹H NMR (CDCl₃): δ 7.74 (s, 1 H, ArOH), 7.26 (dd, *J* = 1.2, 7.8 Hz, 1 H, ArH), 6.90 (d, *J* = 6.9 Hz, 1 H, ArH), 6.80 (t, *J* = 7.5 Hz, 1 H, ArH), 4.86 (s, 2 H, ArCH₂), 1.44 (s, 9 H, ^tBu).

5-*tert*-Butyl-2-hydroxybenzyl alcohol. This compound was synthesised from 5-*tert*-butyl-2-hydroxybenzaldehyde (3.77 g, 21.2 mmol) and NaBH₄ (1.60 g, 42.4 mmol) in MeOH (50 cm³) using a similar procedure as described for 3,5-di-*tert*-butyl-2-hydroxybenzyl alcohol. The product was isolated as a colourless liquid. Yield: 3.74 g (98%). ¹H NMR (CDCl₃): δ 7.23 (dd, *J* = 2.1, 8.3 Hz, 1 H, ArH), 7.10 (bs, 1 H, ArOH), 7.05 (d, *J* = 2.4 Hz, 1 H, ArH), 6.82 (d, *J* = 8.1 Hz, 1 H, ArH), 4.85 (s, 2 H, ArCH₂), 1.28 (s, 9 H, ^tBu).

3. Synthesis of mono- and di-*tert*-butyl substituted 2-hydroxybenzyl bromides

3,5-Di-*tert*-butyl-2-hydroxybenzyl bromide. To a solution of 3,5-di-*tert*-butyl-2-hydroxybenzyl alcohol (3.44 g, 14.6 mmol) in CHCl₃ (50 cm³) was added PBr₃ (0.7 cm³, 7.3 mmol). White fumes appeared immediately during the addition and stirring was continued for 1 h at room temperature. Then cold water (30 cm³) was added with vigorous stirring for 2 min. The organic layer was separated and the aqueous residue was extracted with CHCl₃ (2 × 50 cm³). The combined extracts were dried over anhydrous MgSO₄, concentrated and dried *in vacuo* to give a pale yellow liquid, which was used without further purification. Yield: 4.23 g (97%).

3-*tert*-Butyl-2-hydroxybenzyl bromide. This compound was synthesised from 3-*tert*-butyl-2-hydroxybenzyl alcohol (4.22 g, 23.4 mmol) and PBr₃ (1.1 cm³, 11.7 mmol) in CHCl₃ (50 cm³) using a procedure similar to that for the preparation of 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide. The product was obtained as a pale yellow liquid. Yield: 5.57 g (98%).

5-*tert*-Butyl-2-hydroxybenzyl bromide. This compound was synthesised from 5-*tert*-butyl-2-hydroxybenzyl alcohol (3.74 g, 20.8 mmol) and PBr₃ (1.0 cm³, 10.4 mmol) in CHCl₃ (50 cm³) using a procedure similar to that for the preparation of 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide. The product was obtained as a pale yellow liquid. Yield: 4.95 g (98%).

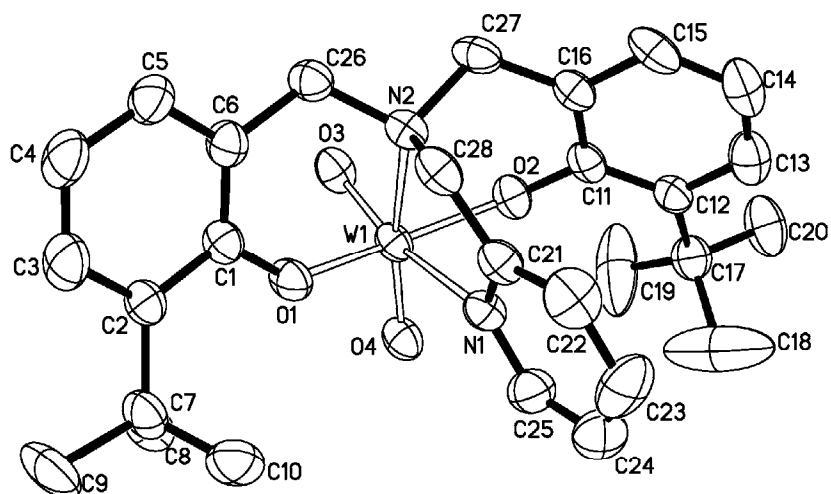


Figure S1. Molecular structure and atom labelling scheme for [WO₂(L²)].
Hydrogen atoms are omitted for clarity.