Supporting Information

Aqueous Phase Organometallic Catalysis Using $(MeCp)_2Mo(OH)(H_2O)^+$. Intramolecular Attack of Hydroxide on Organic Substrates.

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Norborenyl acetate hydrolysis. A solution containing 0.0150 g (16.9 μmol) of $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2][OTs^-]_2$ in 10 mL D_2O was prepared. A 1 mL aliquot of this solution was mixed with 100 μL (873 μmol) of norborenyl acetate (**NA**) in an NMR tube. The resulting solution was bright green and was heated at 80 °C for 3 days. The hydrolysis to form norbornenol (**NOL**) and acetic acid was monitored by NMR spectroscopy. ^{1}H NMR (300 MHz, D_2O): resonances for **NA**, δ 6.32, 6.2, 5.95, 5.35, 4.7, 3.15, 2.85, 2.2-2.1, 2.05, 1.95, 0.9; new resonances for NOL: δ 6.1, 5.9, 5.8, 5.62, 4.42, 3.8, 2.95, 2.66, 1.75. ^{13}C NMR(D_2O): resonances for **NA**, δ 171, 138, 132, 75, 47.6, 46, 42, 34.6, 20.7; new resonances for **NOL** δ 141, 140, 131, 72, 47, 45, 42.7, 35.5. Solutions of pure **NOL** and **NA** in D_2O were used to confirm the NMR assignments. As calculated from the NMR data, approximately 5% of the ester hydrolyzed over 3 days.

Butyl butyrate hydrolysis. A solution containing 0.0150 g (16.9 μmol) of $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2][OTs^-]_2$ in 10 mL of D_2O was prepared. A 1 mL aliquot of this solution was mixed with 50μL (302 μmol) of butyl butyrate in an NMR tube. The resulting solution was heated at 80 °C for 3 days. The hydrolysis to form butanol and butyric acid was monitored by NMR spectroscopy. ^{1}H NMR(300 MHz, D_2O): δ 0.98 (3H, t, $CH_3CH_2CH_2C(O)OH$), 0.96 (3H, t, $CH_3CH_2CH_2CH_2OH$), 1.6 (2H, $CH_3CH_2CH_2C(O)OH$), 1.43 (2H, $CH_3CH_2CH_2CH_2OH$), 2.47 (2H, t, $CH_3CH_2CH_2C(O)OH$), 1.66 (2H, $CH_3CH_2CH_2CH_2OH$), and 3.56 (2H, t, $CH_3CH_2CH_2CH_2OH$).

Vinyl acetate hydrolysis. A solution containing 0.0150 g (16.9 μmol) of [Cp′$_2$Mo(μ-

$OH)_2MoCp'_2][OTs^-]_2$ in 10 mL of D_2O was prepared. A 0.9 mL aliquot of this solution was mixed with 100μL (1.08 mmol) of vinyl acetate in an NMR tube. The resulting solution was heated at 80 °C for 3 days. Before heating, the ^1H NMR (300 MHz, D_2O) showed resonances at δ 7.2 (1H, q, $CH_3C(O)OC\mathit{H}CH_2$), 5.01 (1H, d, $CH_3C(O)OCHC\mathit{H}_2$), 4.76 (1H, d, $CH_3C(O)OCHC\mathit{H}_2$), and 2.17 (3H, s, $C\mathit{H}_3C(O)OCHCH_2$). After heating, additional resonances for acetic acid and acetaldehyde appeared; ^1H NMR(300 MHz, D_2O): δ 2.08 (3H, s, $C\mathit{H}_3C(O)OH$), 9.71 (1H, s, $CH_3C(O)\mathit{H}$), and 2.17 (3H, s, $C\mathit{H}_3C(O)H$).

Methyl cyanoacetate hydrolysis/hydration. A catalyst stock solution was prepared by adding $[Cp'_2Mo(\mu\text{-}OH)_2MoCp'_2][OTs^-]_2$ (0.1128 g, 127 μmol) to 25 mL D_2O. Methyl cyanoacetate (100 μL, 1.13 mmol) was added to 500 μL (2.55 μmol) of the stock solution and the solution was then sealed in a screw-cap NMR tube. The resulting solution was a light pink color. The ^1H NMR spectrum (D_2O) before heating showed a resonance at δ 3.82 (s, 3H, $NCCH_2CO_2C\mathit{H}_3$). The sample was heated in an oil bath at 75 °C for 13 days. During the reaction, intense resonances for methanol and acetamide appeared: δ 3.35 (br, s, 3H, CH_3OH) and 2.05 (m, $C\mathit{H}D_2CONH_2$). After heating, the ^{13}C NMR spectrum (D_2O) showed the following resonances: δ 167.7 (s, $NCCH_2\mathit{C}O_2CH_3$), 115.7 (s, $N\mathit{C}CH_2CO_2CH_3$), 53.9 (s, $NCCH_2CO_2\mathit{C}H_3$), and 49.0 (s, $C\mathit{H}_3OH$). The ^2H NMR spectrum (D_2O) showed resonances at δ 3.59 (s, 3D, CD_3OH) and 1.88 (s, 3D, CD_3CONH_2). When opened, the tube released gas and the solution bubbled. The resulting pH of the solution was 2.08.
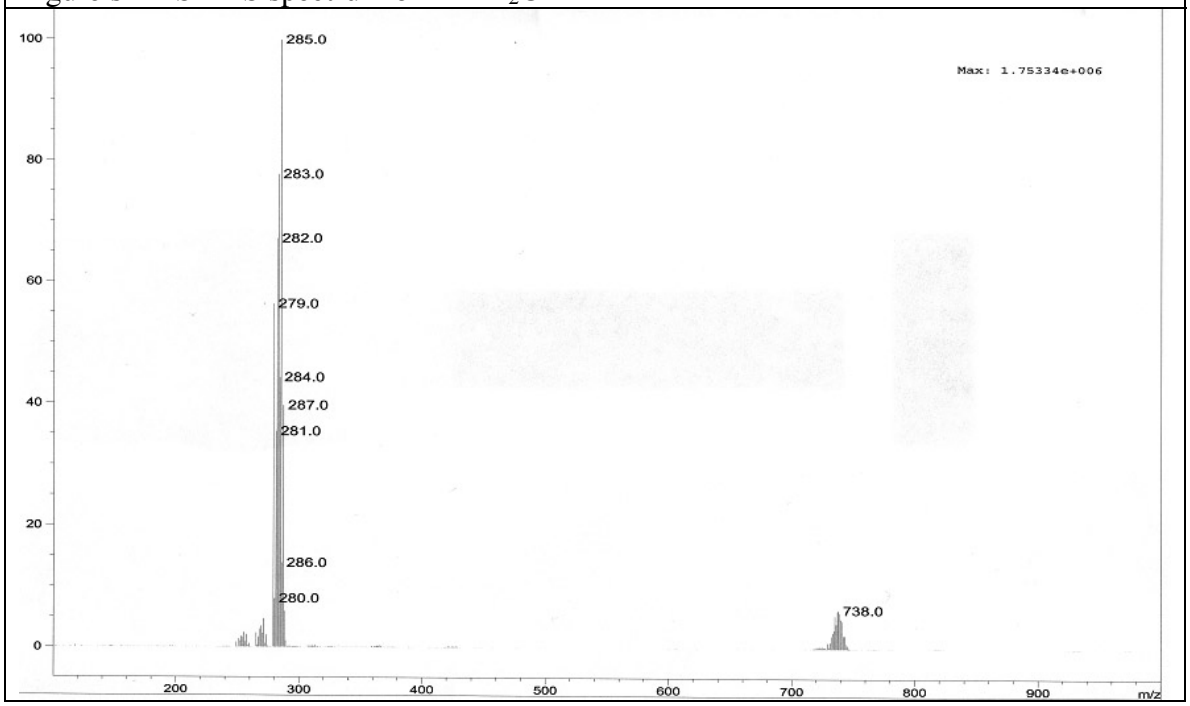
Figure s1: ESI-MS spectrum of **2** in D_2O.