Supporting information

Reactions of the amido hydrido complex of osmium, OsH(NH2CH2CMe2NH2)(PPh3)2: HX addition, HX transfer and ketone H2-hydrogenation.

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OsHCl(tmen)(PPh3)2 (1). Under argon, OsHCl(PPh3)3 (150 mg, 0.148 mmol) and 2,3-diamino-2,3-dimethylbutane (20 mg, 0.172 mmol) were refluxed in THF (5 mL) for 1 h. The solvent was removed from the yellow solution and the residue was stirred in 1:1 ether:hexanes (6 mL). The yellow solid was filtered, washed with ether and dried under vacuum. X-ray structure quality single crystals were obtained by allowing hexanes to slowly diffuse into a concentrated THF solution. Yield: 100 mg (78%). 1H NMR (CD2Cl2) δ: 7.0 - 7.6 (m, phenyl, 30 H), 3.1 (d, NH, 2 H, JHH = 10.8 Hz), 2.5 (d, NH, 2 H), 1.04 (s, CH3, 6 H), 1.02 (s, CH3, 6 H), -20.9 (t, OsH, 1 H, Jhp = 18.4 Hz). 31P {1H} NMR (CD2Cl2) δ: 17.9 (s). IR (nujol) (cm⁻¹): 3310 (ν N-H), 3211 (ν N-H), 3048 (ν N-H), 2101 (ν Os-H). Anal. Obsd: C, 58.26, H, 5.65, N, 3.12. Calcd: C, 58.15, H, 5.46, N, 3.23.

OsH(NH2CH2CMe2NH2)(PPh3)2 (2). Under argon, OsHCl(tmen)(PPh3)2 (77 mg, 0.089 mmol) and KOTBu (12 mg, 0.107 mmol) were stirred in THF (3 mL) for 30 min. The arrange solution was filtered through celite and then the solvent was removed. The residue was stirred in hexanes and filtered, washed with ether and dried under vacuum yielding an orange solid. X-ray structure quality single crystals were obtained by allowing hexanes to slowly diffuse into a concentrated THF solution. Yield: 50 mg (68%). 1H NMR (CD2Cl2) δ: 6.8 - 7.9 (m, phenyl, 30 H), 4.9 (s, NH, 1H), 3.3 (s, NH, 1H), 2.2 (s, NH, 1H), 0.7 (s, CH3, 12 H), -23.7 (broad, OsH, 1 H). 31P {1H} NMR (CD2Cl2) δ: 17.9 (s). IR (nujol) (cm⁻¹): 3306 (ν N-H), 3211 (ν N-H), 3048 (ν N-H), 2101 (ν Os-H). Anal. Obsd: C, 60.26, H, 5.65, N, 3.12. Calcd: C, 60.15, H, 5.58, N, 3.37.

OsH(CNCHCN)(tmen)(PPh3)2 (3). Under argon, 2 (57 mg, 0.069 mmol) and malononitrile (10 mg, 0.151 mmol) were dissolved in toluene (2 mL) and stirred for 20 min. Hexanes were added to precipitate a yellow powder, which was filtered, washed with ether and dried under vacuum. X-ray structure quality crystals were obtained by allowing hexanes to slowly diffuse into a concentrated THF solution. Yield: 50 mg (81%). 1H NMR (C6D6) δ: 6.7 - 7.8 (m, phenyl, 30 H), 2.5 (s, NH, 4 H), 0.5 (s, CH3, 12 H), -15.9 (t, OsH, 1 H, Jhp = 18.1 Hz). 31P {1H} NMR (C6D6) δ: 19.7 (s). IR (nujol) (cm⁻¹): 3315 (ν N-H), 3216 (ν N-H), 3143 (ν N-
OsH₂(tmen)(PPh₃)₂. This complex was observed by ¹H and ³¹P {¹H} NMR by putting a solution of OsH(NHCMe₂CMe₂NH₂)(PPh₃)₂ in C₆D₆ under hydrogen gas. The reaction produced a colour change from orange to yellow. ¹H NMR (C₆D₆) δ: 6.8-8.3 (m, phenyl, 30H), 2.8 (s, NH, 4H), 0.62 (s, CH₃, 6H), 0.63 (s, CH₃, 6H), -6.8 (t, OsH, 2H, J₇-H₉ = 12 Hz). ³¹P {¹H} NMR (C₆D₆) δ: 36.8 (s, PPh₃, 2P).

Hydrogenation of acetophenone using MH(NHCMe₂CMe₂NH₂)(PPh₃)₂ (M = Ru, Os). Under argon, the appropriate amounts of catalyst and acetophenone stock solutions, in benzene, were measured into a 5 mL volumetric flask and diluted to the mark with benzene to give a catalyst concentration of 4.8 x 10⁻⁴ M and an acetophenone concentration of 1.664 x 10⁻¹ M. This solution was immediately transferred by syringe, against a flow of dihydrogen, into a high-pressure reactor in a constant temperature bath set at 20°C. The reactor was degassed with hydrogen gas and set to 5 atm. The solution was stirred under these conditions taking aliquots by syringe at 60, 180, 300, 600, and 1200 seconds. The aliquots were analyzed by gas chromatography and conversion determined by integration of the gas chromatogram.
Integration of the methyl peaks of acetophenone and 1-phenylethanol was used to determine a conversion of 16%.