Supplementary Material

A New Approach to Promoting Sluggish Diels-Alder Reactions: Dihapto-Coordination of the Diene

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General. All reactions were performed in a Vacuum Atmospheres Co. glove box. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova-300, Varian Inova-500, or GN-300 spectrometer at room temperature unless otherwise noted. Chemical shifts are reported in relative to TMS (tetramethylsilane) using residual protonated solvent (acetonitrile- d_2 , δ 1.94) as an internal standard. Two dimensional NMR experiments (gDQCOSY, gHSQC, gHMBC, NOE) were recorded on a Varian Inova-300 or Varian Inova-500 spectrometer. Cyclic voltammograms were recorded in a standard three-electrode cell from +1.7 to -1.7 V utilizing a glassy carbon electrode. All potentials are reported versus NHE and, unless otherwise noted, were determined in CH_3CN (~0.5 M tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mV/s using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) *in situ* as a calibration standard. Infrared spectra were recorded on a MIDAC Prospect (Model PRS) spectrometer as a glaze using a Horizontal Attenuated Total Reflectance Accessory (HATR, Pike Industries). Elemental analyses were performed on a PE2400 Series II CHN analyzer.

Solvents and reagents. All solvents were purified via distillation under nitrogen or passage through an activated alumina column under inert atmosphere and purged with nitrogen prior to use. Acetonitrile- d_3 (Cambridge Isotope Labs) was distilled over CaH_2 under an inert atmosphere prior to use. Ethyl vinyl ketone, methyl vinyl ketone, 3-penten-2-one, mesityl oxide, methacrolein, and methyl acrylate were purchased from Sigma-Aldrich and used without further purification.

TpMo(NO)(MeIm)(η^2 -(1-bicyclo[2.2.2]oct-5-en-2-yl-propan-1-one)) (2)

A solution of $\text{TpMo(NO)(MeIm)(}\eta^2\text{-1,3-cyclohexadiene)}$ (1.08 g, 2.15 mmol) and ethyl vinyl ketone (1.06 g, 12.60 mmol) was prepared in CH_2Cl_2 (2 mL). The solution was allowed to cool to -40°C for 10 min at which time a -40°C solution of $\text{BF}_3\cdot\text{OEt}_2$ (0.180 g, 0.76 mmol) in 1 mL CH_2Cl_2 was added, and the reaction vessel was agitated to mix the solutions together. After 30 min, pyridine (0.53 g, 6.71 mmol) was added and the solution was allowed to warm to room temperature. The solution was subjected to column chromatography with the light-yellow product band being eluted with a 1:3 THF:diethyl ether solution (100 mL). Volatiles were removed *in vacuo* and the light yellow solid was collected in 60% overall yield by precipitation of a THF solution (15 mL) into pentane and collected on a fine porosity fritted glass disc. NMR shows ~1.5:1 ratio of two major diastereomers. (Presumably, the minor isomers include the two exo-cycloadduct-containing complexes, but their presence was not confirmed.)

CV (DMAc) (TBAH) (100 mV/s) $E_{p,a} = -0.280$ V (NHE). IR (HATR, glaze): $\nu(\text{BH}) = 2477\text{ cm}^{-1}$ $\nu(\text{NO}) = 1560\text{ cm}^{-1}$ $\nu(\text{CO}) = 1702\text{ cm}^{-1}$. ^1H NMR (mixture of isomers) (300 MHz) (d_6 -acetone) (22°C) δ 7.82 (7 H, m, Tp), 7.50 (2H, br s, Tp), 7.29 (2H, br s, Tp), 7.16 (3H, m, Tp or Im), 6.69 (1H, s, Im), 6.67 (1H, s, Im), 6.23 (2H, t, $J=2$ Hz, Tp 4), 6.18 (2H, overlapping t, $J=2$ Hz, 2Hz, Tp 4), 3.77 (3H, s, N-Me), 3.76 (3H, s, N-Me), 2.98 (2H, br m), 2.83 (1H, br m), 2.68 (1H, br s), 2.47, 2.45 (7H overlapping, each a q, Et CH_2), 2.29 (1H buried, m), 2.21 (3H buried, m), 1.81 (3H, m), 1.48 (4H, m), 0.95 (5H, t, Et CH_3), 0.83 (2H, t, Et CH_3). ^{13}C NMR (mixture of isomers) (300 MHz) (d_6 -acetone) (22°C) δ 211.9 (CO), 211.5 (CO), 144.6, 144.5, 141.2, 140.6, 140.4, 138.9, 136.3, 135.5, 135.4, 134.7, 134.6, 129.7, 121.7, 121.6

(14x1C, Tp and Im), 105.8, 105.7, 105.5 (3x1C, Tp 4), 77.2, 73.6, 71.1, 67.5, 54.1, 53.6, 36.6, 33.8, 33.7, 33.2, 33.0, 31.9., 31.6, 28.3, 26.9. 26.0, 8.1, 7.9. Anal. Calcd. For $C_{24}H_{32}BMoN_9O_2$: C, 49.25; H, 5.51; N, 21.54. Found: C, 49.46; H, 5.50; N, 21.39.

General Procedure for Cycloaddition Reactions in Methylene Chloride

A solution of complex **1** (0.20 g, 0.40 mmol) and unsaturated carbonyl (5 eq.) was prepared in CH_2Cl_2 (~0.5 mL). The Solution was cooled to $-40\text{ }^{\circ}C$ for 5 minutes at which time a cold ($-40\text{ }^{\circ}C$) solution of $BF_3 \cdot OEt_2$ in CH_2Cl_2 (~0.5 mL) was added. The reaction vessel was agitated to mix the solutions. After the reaction finished (usually 30 minutes), pyridine (5 eq.) was added and the reaction mixture was allowed to warm to room temperature. The mixture was filtered through a silica plug (~4 cm), washed with 1 : 3 THF : Et_2O (~75 mL), and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (~2 mL) and was stirred with AgOTf (1.1 eq.) or in air for 1 hour. Pentane (~2 mL) was added to the reaction mixture and then the mixture was filtered through a silica pad, washed with 1 : 1 CH_2Cl_2 : pentane (~6 mL). The filtrate was concentrated and subjected to preparatory thin-layer chromatography eluted with 10% EtOAc in hexanes. The product bands were cut out, extracted with $CHCl_3$, and evaporated to get the final products. Yields were determined by from proton NMR data of the crude mixture before chromatography using durene as integration standard.

General Procedure for Cycloaddition Reactions in Methanol

A solution of complex **1** (0.10 g, 0.20 mmol) and unsaturated carbonyl (5 eq.) was prepared in ~0.4 mL of CH_2Cl_2 . Then methanol (~0.4 mL) was added and the reaction mixture was stirred at room temperature for 4 days. The mixture was filtered through a silica plug (~4 cm), washed with THF (1 mL _ 3), and the filtrate was concentrated in vacuo. The residue was dissolved in acetone- d_6 (~0.5 mL) and was stirred in air for 1 hour. Yields were determined by from proton NMR data using durene as integration standard.

1-(7,7-Dimethylbicyclo[2.2.2]oct-2-en-8-yl)ethanone (**6**)

endo: 1H NMR ($CDCl_3$, 300 MHz, $25^{\circ}C$): δ 6.27 (m, 2H, 2, 3), 2.56 (m, br, 1H, 4 (bridgehead)), 2.43 (s, br, 1H, 8), 2.07 (s, 3H, $COCH_3$), 2.02 (m, br, 1H, 1 (bridgehead)), 1.87 (m, 1H, 5a), 1.41 (m, 1H, 6a), 1.28 (s, 3H, 11- CH_3), 1.21 (m, 1H, 5b), 1.09 (m, 1H, 6b). ^{13}C NMR ($CDCl_3$, 75MHz, $25^{\circ}C$): δ 210.6, (CO), 134.1 (C3), 131.6 (C2), 63.9 (C8), 43.6 (C1), 39.2 (C7), 33.1 (C4), 31.5 (C10), 30.7 (C11), 25.9 (C12), 25.2 (C6 or C5), 20.3 (C6 or C5). Stereochemical assignments of the two diastereomers for **6** were made using NOESY data, which for the *endo* isomer show an interaction between the olefinic proton H3 and the acetyl methyl group.

LRMS (EI): m/z = 43, 80 (100%), 99, 178 (M⁺). IR (glaze, cm^{-1}): 1707 (vs,CO), 2965 (s), 2871 1365, 1353.

exo: (only partial characterization due to low concentration) 1H NMR ($CDCl_3$, 300 MHz, $25^{\circ}C$): δ 6.30 (dd, 1H, J = 6.0, 6.0 Hz, 3), 6.20 (dd, 1H, J = 6.0, 6.0 Hz, 2), 2.63 (m, br, 1H, 4 (bridgehead)), 2.18 (s, br, 1H, 8), 2.11 (s, 3H, $COCH_3$), 1.96 (m, br, 1H, 1 (bridgehead)), 1.09 (s, 3H, 11- CH_3), 1.00 (s, 3H, 12- CH_3), 5a, 5b, 6a and 6b were not identified.

(A weak resonance at 92.0 ppm does not correlate with any proton for **6** (HSQC) and is thought to be trace CCl_4).

^{13}C Spectrum for compound 6:

^1H NMR spectrum for compound 6: