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Development of new transition metal catalysts for the oxidation of a hydroxamic acid with *in situ* Diels-Alder trapping of the acyl nitroso derivative.

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Experimental

General experimental

All ^{1}H NMR spectra were recorded on the 400 MHz spectrometer and shifts recorded with the reference to TMS. ^{13}C NMR spectra were recorded on the 100 MHz spectrometer. Column chromatography was performed on silica gel, 60 mesh. TLC was performed on plastic backed silica gel plates with visualization achieved using a UV lamp or staining with K_2MnO_4 solution. All materials were purchased directly from standard chemical suppliers and used without further purification, unless stated otherwise.

Preparation of μ-alkoxo-(1-[(2-hydroxy-3,5-di-*tert*-butyl-benzylidene)-amino]-indan-2-ol)iron(III) chloride complex 5

Anhydrous iron(III) chloride (73 mg, 0.45 mmol) was added in one portion to a stirred solution of (1*S*,2*R*)-1-[(2-hydroxy-3,5-di-*tert*-butylbenzylidene)amino]indan-2-ol (150 mg, 0.41 mmol) and Et_3N (126 μL, 0.90 mmol) in DCM (10 mL); the reaction mixture turning brown. After 12 hours at RT, DCM (10 mL) was added, the reaction mixture was washed with brine (2 x 30 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to approximately half of its volume and then layered with petroleum ether (40 – 60°). Crystals suitable for single crystal analysis formed at the bottom of the reaction flask following slow diffusion of the solvents over *ca*. 2 days at 20 °C. The crystals were collected and dried *in vacuo* to give product **5** (153 mg, 81 %) as a brown crystals; mp > 220 °C; Found (%): C 63.06, H 6.50, N 2.19 ($C_{48}H_{58}Cl_2Fe_2N_2O_4$ requires C 63.38, H 6.43, N 3.08); ν_{max}/cm^{-1} 2958m, 1614vs (C=N stretch), 1538m, 1460m, 1429m, 1389m, 1362w, 1336w, 1304w, 1273w, 1253m, 1199w, 1175m, 1094m, 1047m, 864w, 844w, 748m, 643w, 614w, 542m; m/z (FB) 908.2470 (M$^+$ for $C_{48}H_{58}Cl_2Fe_2N_2O_4$ requires 908.2467), 873 (15), 784 (100), 419 (15); λ_{max}(DCM)/nm (ε / mol^{-1}cm^{-1}dm^3) 501 (3363), 324 (11966), 272 (31226), 239 (30588), 224 (37546).

Preparation of (1-[(2-hydroxy-3,5-di-*tert*-butyl-benzylidene)-amino]-indan-2-ol)ruthenium(III) p-cymene chloride complex 6

(1*S*,2*R*)-1-[(2-hydroxy-3,5-di-*tert*-butylbenzylidene)amino]indan-2-ol (100 mg, 0.27 mmol) and di-*μμ*-chlorobis(*p*-cymene)chlororuthenium(II) (84 mg, 0.14 mmol,) were dissolved in dichloromethane (5 mL). The mixture was then treated with Et_3N (76 μL, 0.55 mmol) and the reaction monitored by TLC (petroleum ether:ethyl acetate as eluent, 4:1) for the consumption of the ligand. After 15 minutes, the mixture was poured into water (15 ml), the organic layer was separated, dried ($MgSO_4$) and evaporated. The crude residue was redissolved in ether and the product precipitated by slow addition of n-hexane. A brown-red solid **6** was collected by filtration and dried *in vacuo* (79 mg, 48 %); m.p. > 220 °C; Found (%): C 63.30, H 6.99, N 2.19 ($C_{34}H_{43}ClNO_2Ru\cdot{}^1/_2H_2O$ requires C 63.49, H 6.89, N 2.18); ν_{max}/cm^{-1} 3380m (br), 2959s, 1612vs, (C=N stretch), 1532m, 1459m, 1438m, 1410m, 1386m, 1361m, 1334m, 1293w, 1272w, 1254m, 1200w, 1170m, 1096w, 1055w, 917w, 873w, 843w, 802w, 780w, 743m, 637w, 592w, 532w; ^{1}H NMR 400 MHz, $CDCl_3$: δ_H 1.13 (9H, s, ^{t}Bu^1)1.32 (3H, d, J = 7.2, ^{i}CH_3), 1.33 (3H, d, J = 6.8, ^{i}CH_3), 1.47 (9H, s, ^{t}Bu^2), 2.33 (3H, s, PhCH_3), 2.92 (1H, m, J = 6.8, ^{i}C*H*), 3.23 (1H, dd, J_1 = 17.2, J_2 = 6.0, OCHC*H*HC), 3.67 (1H, m, OCHCH*H*C), 4.98 (2H, m, OC*H*CH$_2$C and p-cy*H1*), 5.35 (1H, d, J = 6.4, p-cy*H2*), 5.53 (1H, d, J = 6.0, p-cy*H3*), 5.56 (1H, d, J = 6.0, p-cy*H4*), 6.04 (1H, d, J = 6, NC*H*CHOCH$_2$), 6.52 (1H, d, J = 2.4, NCHC*H*C^{t}Bu), 7.22 (1H, d, J = 7.2, InAr-*H1*), 7.26 – 7.41 (4H, br m, InAr-*H2-4* and ^{t}BuCCHC^{t}Bu), 7.72 (1H, s, C*H*NAr); ^{13}C NMR, $CDCl_3$: δ_C 19.1, 21.9, 23.6, 29.7, 30.9, 31.3, 33.7, 35.4, 38.4, 72.2, 80.8, 81.8, 82.4, 84.9, 88.1, 99.8, 99.9, 116.9, 124. 8, 126.5, 127.1, 128.4, 129.4, 130.5, 135.0, 139.7, 139.9, 142.5, 162.5, 165.6; *m/z* (FB) 635.2094 ([M+H]$^+$ $C_{34}H_{43}ClNO_2Ru$ requires 635.2099), 600 (100), 501 (18), 465 (25); λ_{max}(DCM)/nm (ε / mol^{-1}cm^{-1}dm^3) 490 (682), 441 (1167), 364 (1656), 303 (3818), 255 (14505), 223 (19116).

Screening procedure

Catalyst (0.1 mol%) and hydroxamic acid (0.30 mmol) were dissolved in the solvent (3 mL) (either acetone or DCM depending on oxidant used, see Table 2 in main paper) and stirred at RT for 5 minutes. Then diene (0.33 mmol) was added and the reaction was stirred for a further 5 minutes. Finally, the mixture was treated by dropwise addition with the oxidant (either hydrogen peroxide or *tert*-butyl hydrogen peroxide) (0.36 mmol). The reaction mixture was then stirred for further 16 hours at room temperature after which it was diluted with DCM (15 mL) and washed firstly with water (2 x 30 mL) then brine (2 x 30 mL). Organic phase was collected, dried ($MgSO_4$) and concentrated *in vacuo*. The cycloadducts were purified by silica gel chromatography (petroleum ether:ethyl acetate as eluent, 9:1) to give the yields reported in **Table 2**.

X-ray Crystallography

A dark red single crystal of **5** (0.02 x 0.08 x 0.20 mm) was analysed at 120(2)K on a Bruker SMART-CCD 1K area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Structure solution was carried out using SHELXS-97[1] and refined using full matrix least squares in SHELXL-97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned geometrically with isotropic displacement parameters fixed to ride on the parent atom (aromatic C-H 0.94 Å, $U_{iso} = 1.2 \times U_{eq}(C)$; methyl C-H 0.98 Å, $U_{iso} = 1.5 \times U_{eq}(C)$; methylene C-H 0.99 Å, $U_{iso} = 1.2 \times U_{eq}$ (C)). The asymmetric unit consisted of one molecule of the iron complex **5** along with a molecule of dichloromethane solvent at 30% occupancy. Crystal data for **5**: M = 935.04, orthorhombic space group $P\ 2_12_12_1$, a = 12.370(3), b = 17.427(2), c = 22.378(5) Å, V = 4824.0(15) Å^3, Z = 4, D_c = 1.287 Mg/m^3, μ = 0.788 mm^{-1}, $F(000)$ = 1962, 23875 reflections collected ($1.48 \le \theta \le 26.36°$), 9356 independent reflections (R_{int} = 0.0616) used for structure refinement, final R_1 = 0.0553 [$F^2 > 2\sigma(F)$], wR_2 = 0.1096 [$F^2 > 2\sigma(F)$], R_1 = 0.0824 (all data), wR_2 = 0.1201 (all data), GOF (F^2) = 1.067, largest peak, hole = 0.658, -0.681 e Å^{-3}. CCDC reference number 642155. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704728b.

References

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 1990, **A46**, 467–473.
2. G. M. Sheldrick, *Computer Program for Crystal Structure Refinement,* University of Göttingen.