Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Synthesis and Structural Characterization of *Tris*(2-oxo-1-t-butylimidazolyl) and *Tris*(2-oxo-1-methylbenzimidazolyl)hydroborato Complexes: A New Class of Tripodal Oxygen Donor Ligand

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EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen or argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 DRX, Bruker 400 AVIII, Brucker 400 Cyber-enabled Avance III and Bruker Avance 500 DMX spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H; 7.26 for $CHCl_3$ and 2.50 for d_6-DMSO).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for $CDCl_3$, 128.06 for C_6D_6, 54.00 for CD_2Cl_2 and 39.52 for d_6-DMSO).[2] Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm^{-1}. Mass spectra were obtained on a Jeol JMS-HX110H Tandem Double-Focusing Mass Spectrometer with a 10 kV accelerated voltage equipped with FAB ion source. 1-*tert*-Butyl-1,3-dihydro-2*H*-imidazol-2-one[3] and 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-one[4] were prepared by the literature methods. $NaBH_4$ (Aldrich), $LiBH_4$ (Strem), ZnI_2 (Aldrich), $CoCl_2$ (Aldrich), $FeCl_2$ (Strem Chemicals), $ZrCl_4$ (Aldrich), $CpZrCl_3$ (Aldrich), $Re(CO)_5Br$ (Strem Chemicals) and 1-methyl-1,3-dihydro-2*H*-benzimidazol-2-thione (Aldrich) were obtained commercially and used as received.

X-ray structure determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.1).[5]

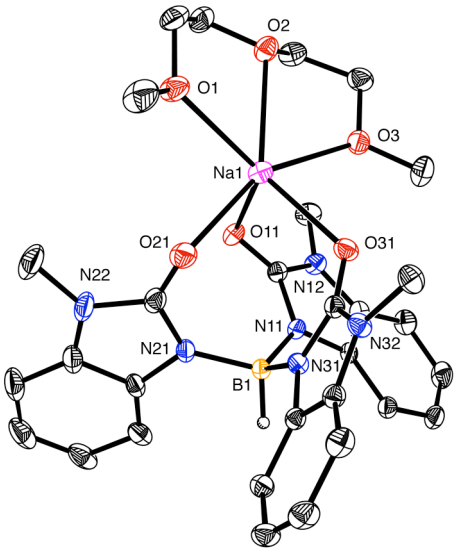
Measurement of Cone Angles

Crystallographic cone angles (Θ) were measured by using the procedure described by Mingos.[6] Specifically, the half-angle (θ_i) for each arm of the ligand is calculated as the maximum value of B•••M•••H, where the hydrogen atom position takes into account the van der Waals radius of hydrogen (1.2 Å). The crystallographic cone angle for the ligand is then defined as $\Theta = (2/3)\,\Sigma\theta_i$.

Synthesis of [To^{MeBenz}]Na

A mixture of 1-methyl-2-benzimidazolinone (700 mg, 4.73 mmol) and $NaBH_4$ (51 mg, 1.35 mmol) was placed in an ampoule and treated with diglyme (*ca.* 10 mL). The mixture was heated at 175 ˚C for 1 week, cooled to room temperature and filtered. The precipitate was washed with pentane (*ca.* 5 mL) and dried *in vacuo*, yielding [To^{MeBenz}]Na•diglyme as a white solid (650 mg, 79%). Analysis calcd. for [To^{MeBenz}]Na•diglyme: C, 59.0%; H, 5.9%; N 13.8%. Found: C, 58.8%; H, 4.9%; N 14.6%. ^{1}H NMR (C_6D_6): 2.74 [s, 9H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 3.10 [s, 6H of 2C$\underline{H}_3$ for diglyme], 3.30 [t, $^3J_{H\text{-}H}$ = 5, 4H of 2C$\underline{H}_2$ for diglyme], 3.43[t, $^3J_{H\text{-}H}$ = 5, 4H of 2C$\underline{H}_2$ for diglyme], 5.40 [b, 1H of $\underline{H}$B{(C_4H_4)C_2N_2(CH_3)CO}$_3$], 6.54 [d, $^3J_{H\text{-}H}$ = 7, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.94 [m, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.59[d, $^3J_{H\text{-}H}$ = 7, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 26.2[3 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 58.7 [2 C, methyl of the diglyme], 70.6 [2 C, methylene of the diglyme], 72.0[2 C, methylene of the diglyme], 106.9 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 111.8 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 120.4 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 121.6[3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 131.9 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 134.8[3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 159.7 [3 C, HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$]. FAB-MS: m/z = 476.3 $[M]^+$, M = [To^{MeBenz}]Na. IR Data (KBr disk, cm^{-1}): 3424 (br), 3054 (w), 2931 (m), 2887 (m), 2425 (w) [ν_{BH}], 1699 (s), 1674 (s), 1602 (m), 1544 (w), 1495 (s), 1433 (s), 1390 (s), 1377 (s), 1316 (m), 1299 (s), 1212 (m), 1160 (m), 1121 (s), 1088 (s), 1017 (m), 853 (m), 768 (s), 736 (s),

693 (m), 669 (w), 620 (m), 564 (m), 511 (m), 445 (m). Colorless blocks of [To^{MeBenz}]Na•diglyme suitable for X-ray were obtained from diglyme.

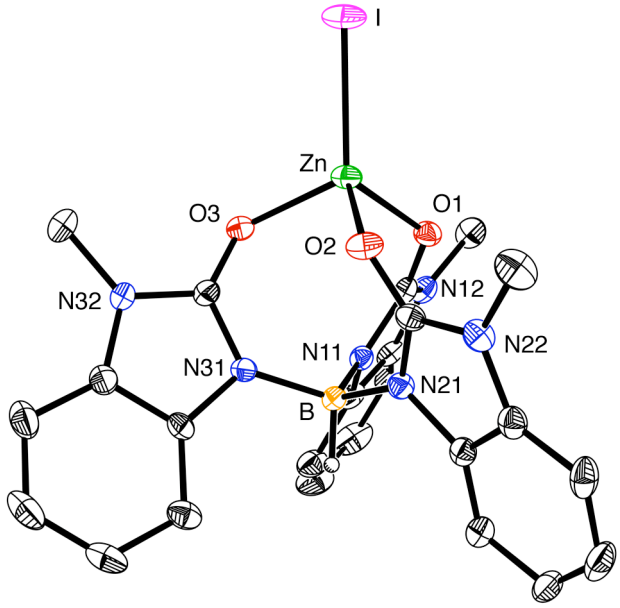


Molecular Structure of [To^{MeBenz}]Na•diglyme

Synthesis of [To^{MeBenz}]ZnI

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and ZnI_2 (21 mg, 0.07 mmol) was treated with dichloromethane (*ca.* 8 mL) resulting in the immediate deposition of a white precipitate. The mixture was stirred for *ca*. 4 hours at room temperature, allowed to settle and then filtered. The filtrate was concentrated to *ca.* 3 mL and treated with pentane (*ca.* 10 mL), thereby resulting in the formation of a precipitate. The mixture was filtered and the volatile components were removed from the filtrate *in vacuo* to give [To^{MeBenz}]ZnI as white powder (20 mg, 47%). Crystals of composition [To^{MeBenz}]ZnI•CH_2Cl_2 suitable for X-ray diffraction were obtained from a solution in dichloromethane. Analysis calcd. for [To^{MeBenz}]ZnI•CH_2Cl_2: C, 41.1%; H, 3.3%; N, 11.5%. Found: C, 41.7%; H, 3.1%; N 11.1. ^{1}H NMR (C_6D_6): 2.48 [s, 9H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 6.37 [d, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.88 – 7.00 [m, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.60 [d, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 26.6 [9 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 109.0 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 112.4 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.1 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.6 [3C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 131.3 [3C,

$HB\{(C_4H_4)\underline{C}_2N_2(CH_3)CO\}_3]$, 133.3[3C, $HB\{(C_4H_4)\underline{C}_2N_2(CH_3)CO\}_3]$, [3C, $HB\{(C_4H_4)C_2N_2(CH_3)\underline{C}O\}_3]$ not observed.

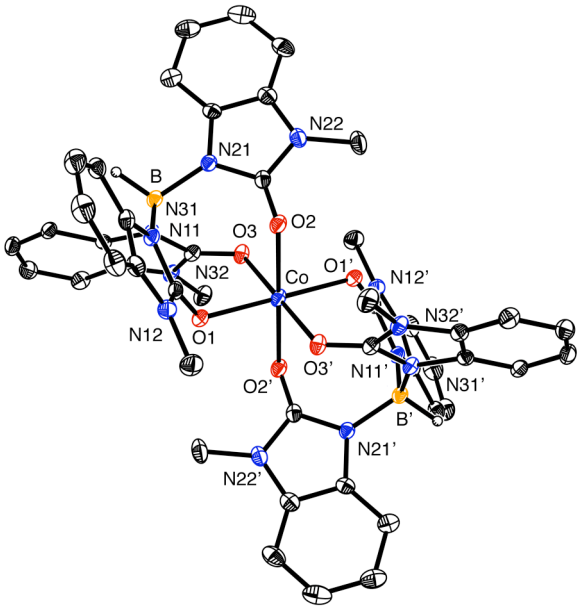


Molecular Structure of [To^{MeBenz}]ZnI

Synthesis of [To^{MeBenz}]$_2$Co

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and $CoCl_2$ (4 mg, 0.03 mmol) was placed in an ampoule, treated with dichloromethane (*ca.* 5 mL) and heated overnight at 60 ˚C. After this period, the volatile components were removed *in vacuo* and the solid residue was washed sequentially with hexane (*ca.* 3 mL) and acetonitrile (*ca.* 5 mL). The residue was extracted into warm chloroform (2 × *ca.* 5 mL) and the volatile components were removed from the extract *in vacuo* to give [To^{MeBenz}]$_2$Co as a lilac powder (20 mg, 67%). Crystals suitable for X-ray diffraction were obtained from a solution in chloroform. Analysis calcd. [To^{MeBenz}]$_2$Co: C, 59.7%; H, 4.6%; N, 17.4%. Found: C, 59.3%; H, 4.1%; N, 16.1 %. μ_{eff} (Evans Method, room temperature): 5.5 μ_B. ^{1}H NMR ($CDCl_3$): -7.01 [s, 18H of $HB\{(C_4H_4)C_2N_2(C\underline{H}_3)CO\}_3]$, 2.07 [d, $^3J_{H\text{-}H}$ = 7, 6H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_3]$, 6.72 [t, $^3J_{H\text{-}H}$ = 7, 6H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_3]$, 8.67 [d, $^3J_{H\text{-}H}$ = 7, 6H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_3]$, 16.75 [t, $^3J_{H\text{-}H}$ = 7, 3H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CO\}_3]$. FAB-MS: m/z = 965.3 $[M]^+$, M = [To^{MeBenz}]$_2$Co. IR Data (KBr disk, cm^{-1}): 3446 (br), 3054 (w), 2927 (m), 2855 (w), 2426 (w) [ν_{BH}], 2228 (w), 1629 (s),

1601 (s), 1544 (w), 1494 (s), 1440 (m), 1397 (m), 1300 (m), 1223 (m), 1148 (m), 1124 (m), 1095 (m), 1013 (w), 996 (w), 847 (m), 771 (m), 735 (m).

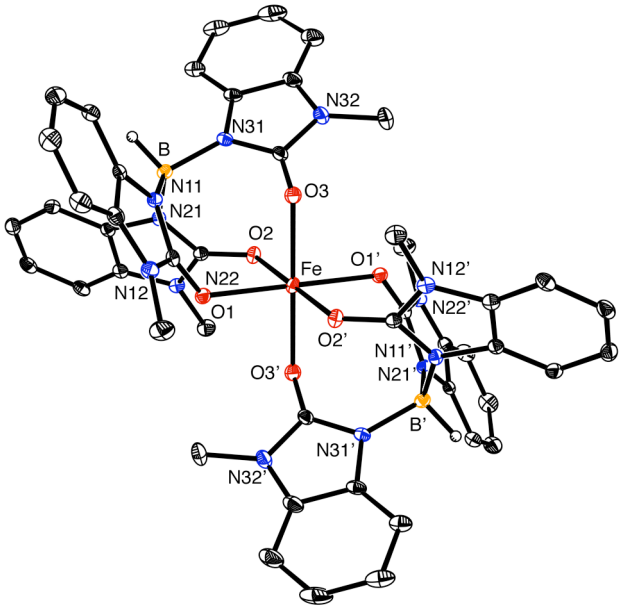


Molecular Structure of [To^{MeBenz}]$_2$Co

Synthesis of [To^{MeBenz}]$_2$Fe

A mixture of [To^{MeBenz}]Na•diglyme (50 mg, 0.08 mmol) and $FeCl_2$ (5 mg, 0.04 mmol) was placed in an ampoule, treated with chloroform (*ca.* 5 mL) and heated overnight at 60 ˚C. After this period, the volatile components were removed *in vacuo* and the solid residue was washed sequentially with hexane (*ca.* 5 mL) and acetonitrile (*ca.* 5 mL). The residue was extracted into warm chloroform (2 × *ca.* 5 mL) and the volatile components were removed from the extract *in vacuo* to give [To^{MeBenz}]$_2$Fe as a very pale powder (24 mg, 61%). Crystals suitable for X-ray diffraction were obtained from a solution in chloroform. μ_{eff} (Evans Method, room temperature): 3.8 μ_B. ^{1}H NMR ($CDCl_3$): -23.3 [s, 18H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 0.5 [br, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.4 [br, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 11.9 [br, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 25.7 [br, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. FAB-MS: m/z = 962.3 $[M]^+$, M = [To^{MeBenz}]$_2$Fe. IR Data (KBr disk, cm^{-1}): 3450 (br), 2923 (m), 2848 (w), 2434 (w) [ν_{BH}], 1637 (s), 1629 (s), 1601 (m), 1544

(w), 1510 (w), 1493 (m), 1440 (m), 1397 (m), 1299 (w), 1219 (w), 1152 (w), 1124 (m), 1094 (w), 1014 (w), 844 (w), 769 (m), 735 (m).

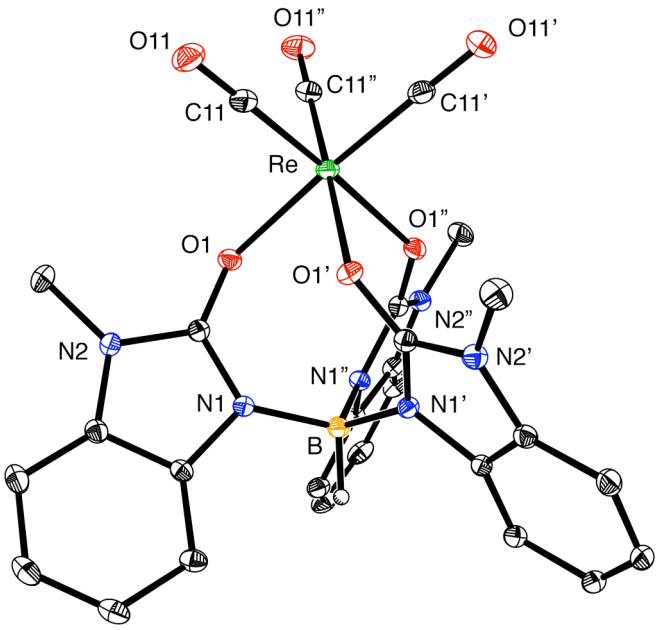


Molecular Structure of [To^{MeBenz}]$_2$Fe

Synthesis of [To^{MeBenz}]Re(CO)$_3$

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and Re(CO)$_5$Br (27 mg, 0.07 mmol) was placed in an ampoule, treated with benzene (*ca.* 5 mL) and heated overnight at 70 ˚C. The reaction mixture was filtered and the volatile components were removed from the filtrate *in vacuo.* The residue obtained was washed with acetonitrile (ca. 5 mL) to give [To^{MeBenz}]Re(CO)$_3$ as white powder (24 mg, 50%). Analysis calcd. for [To^{MeBenz}]Re(CO)$_3$: C, 44.8%; H, 3.1%; N 11.6%. Found: C, 44.6%; H, 3.2%; N 11.4%. ^{1}H NMR (C_6D_6) : 2.81 [s, 9H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 6.37 [d, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.88 [t, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.99 [t, $^3J_{H\text{-}H}$ =8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.57 [d, $^3J_{H\text{-}H}$ =8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 27.0 [3 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 109.1 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 112.2 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.1 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.7 [3C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 131.2

[HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 132.8 [HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 161.0 [HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$]. FAB-MS: m/z = 724.1 $[M]^+$, M = [To^{MeBenz}]Re(CO)$_3$. IR Data (KBr disk, cm^{-1}): 2938 (w), 2457(w) [ν_{BH}], 2022 (s) [ν_{CO}], 1911 (s) [ν_{CO}], 1637 (s), 1588 (s), 1490 (m), 1448 (m), 1399 (m), 1302 (w), 1232 (w), 1158 (w), 1126 (w), 1099 (w), 764 (w). IR Data (CH_2Cl_2, cm^{-1}): 2026 (m) [ν_{CO}], 1894 (s) [ν_{CO}].

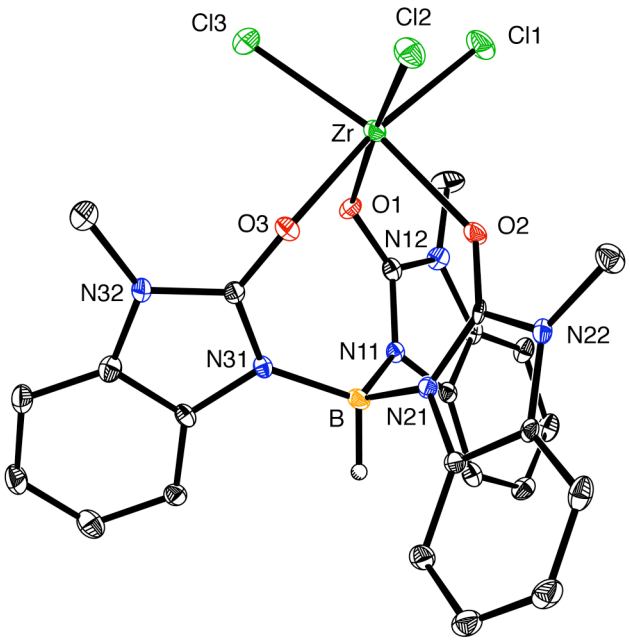


Molecular Structure of [To^{MeBenz}]Re(CO)$_3$

Synthesis of [To^{MeBenz}]ZrCl$_3$

A mixture of [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) and $ZrCl_4$ (18 mg, 0.08 mmol) was placed in an ampoule and treated with dichloromethane (*ca.* 6 mL) and heated overnight at 50 ˚C. After this period, the mixture was filtered and the volatile components were removed from the filtrate *in vacuo.* The solid residue was washed with acetonitrile (*ca.* 3 mL) and hexane (*ca.* 3 mL) to yield [To^{MeBenz}]$ZrCl_3$ as a white powder (14 mg, 33%). ^{1}H NMR (C_6D_6): 2.96 [s, 9H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 6.33 [d, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.85 [t, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.00 [t, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.56 [d, $^3J_{H\text{-}H}$

= 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 28.9 [3 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 109.8 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 113.2 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 123.5 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 123.7 [3C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 128.5 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 130.7 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], [3 C,HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$] not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 29.2 [3 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 110.3 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 113.7 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 123.9 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 124.1 [3C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 131.2 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 132.6 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 158.8 [3 C,HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$]. Analysis calcd. for [To^{MeBenz}]$ZrCl_3$•CH_2Cl_2: C, 40.8%; H, 3.3%; N 11.4%. Found: C, 41.0%; H, 3.4%; N 11.0%.

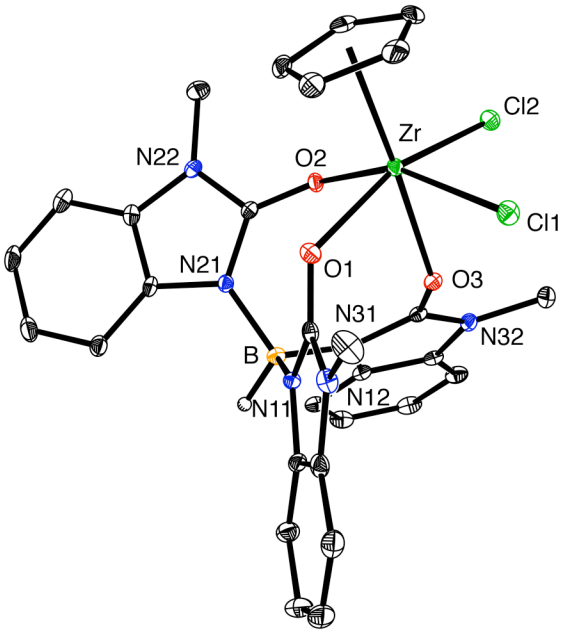


Molecular Structure of [To^{MeBenz}]$ZrCl_3$

Synthesis of Cp[To^{MeBenz}]$ZrCl_2$

A mixture of $CpZrCl_3$ (18 mg, 0.07 mmol) and [To^{MeBenz}]Na•diglyme (40 mg, 0.07 mmol) was placed in an ampoule and treated with benzene (*ca.* 5 mL). The mixture was stirred at room temperature for a period of 2 hours during which it became a suspension. The mixture was treated with *n*-hexane (*ca.* 5 mL) to precipitate more material, which was

isolated by filtration. The precipitate was washed with *n*-hexane, dried *in vacuo*, and then extracted with dichloromethane (*ca*. 5 mL). The volatile components were removed *in vacuo* to give [To^{MeBenz}]$CpZrCl_2$ as a white powder (30 mg, 67%). Crystals suitable for X-ray diffraction were obtained from slow evaporation from a solution in benzene. Analysis calcd. for Cp[To^{MeBenz}]$ZrCl_2$: C, 51.2%; H, 4.0%; N 12.3%. Found: C, 50.8%; H, 3.9%; N 11.3%. ^{1}H NMR (C_6D_6): 2.88 [s, 6H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 3.23 [s, 3H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CO}$_3$], 6.31 [d, $^3J_{H\text{-}H}$ = 8, 1H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.51 [d, $^3J_{H\text{-}H}$ = 8, 2H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.69 [s, 5H of $C_5\underline{H}_5$], 6.78 [t, $^3J_{H\text{-}H}$ = 8, 1H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 6.95 [m, 4H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.06 [t, $^3J_{H\text{-}H}$ = 8, 1H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.48 [d, $^3J_{H\text{-}H}$ = 8, 1H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$], 7.67 [d, $^3J_{H\text{-}H}$ = 8, 2H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 28.0 [2 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 29.1 [1 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CO}$_3$], 109.2 [2 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 109.4 [1 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 111.6 [1 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 112.9 [2 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 118.2 [5 C, $\underline{C}_5H_5$], 122.1 [1 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.4 [1 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 122.6 [2 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 123.1 [2C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CO}$_3$], 131.0 [2C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 131.5 [1C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 132.6 [1C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 133.1 [2C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CO}$_3$], 159.1 [1C, HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$], 159.6 [2C, HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$O}$_3$].



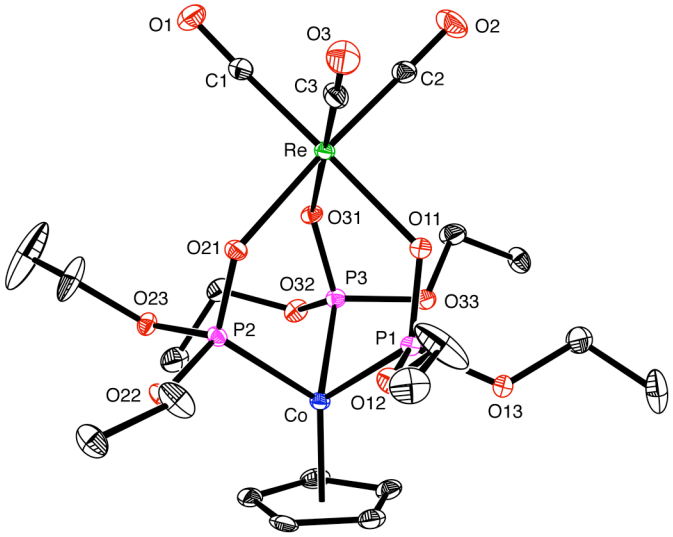
Molecular Structure of Cp[To^{MeBenz}]ZrCl$_2$

Synthesis of [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$

A mixture of [CpCo{P(O)(OEt)$_2$}$_3$]Na (69 mg, 0.12 mmol) and Re(CO)$_5$Br (50 mg, 0.12 mmol) was placed in an ampoule, treated with THF (*ca*. 8 mL) and heated for 3 days at 60 ˚C. After this period, the mixture was filtered and the volatile components were removed from the filtrate *in vacuo*. The residue was washed with hexane and dissolved in benzene for crystallization to yield yellow crystal (40 mg, 41%).

Analysis calcd. [L$_{OET}$]Re(CO)$_3$: C, 29.8% ; H, 4.4%. Found: C, 29.6%; H, 4.1%.

^{1}H NMR (C$_6$D$_6$): 1.15 [t, $^3J_{H\text{-}H}$ = 7, 18 H of C$_5$H$_5$Co{OP(CH$_2$C<u>H</u>$_3$)$_2$}$_3$], 4.07 [m, 12 H of C$_5$H$_5$Co{OP(C<u>H</u>$_2$CH$_3$)$_2$}$_3$], 4.76 [s, 5H of C$_5$<u>H</u>$_5$Co{OP(CH$_2$CH$_3$)$_2$}$_3$]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): ^{13}C{^{1}H} NMR (C$_6$D$_6$): 16.8 [m, 6 C of C$_5$H$_5$Co{OP(CH$_2$<u>C</u>H$_3$)$_2$}$_3$], 61.4 [m, 6 C of C$_5$H$_5$Co{OP(<u>C</u>H$_2$CH$_3$)$_2$}$_3$], 89.3 [s, 5 C of <u>C</u>$_5$H$_5$Co{OP(CH$_2$CH$_3$)$_2$}$_3$]. IR Data (KBr disk, cm^{-1}): 2982 (s), 2903 (m), 2367 (w), 2346 (w), 2013 (vs) [ν_{CO}], 1873 (vs) [ν_{CO}], 1688 (vw), 1656 (vw), 1478 (w), 1441 (m), 1388 (m), 1115 (vs), 1041 (vs), 936 (vs), 839 (s), 776 (s), 740 (s), 671 (vw), 655 (w), 631 (m), 590 (s), 529 (w), 510 (m). IR Data (CH$_2$Cl$_2$, cm^{-1}): 2015 (s) [ν_{CO}], 1880 (s) [ν_{CO}]. MS: *m*/*z* = 806.38 [M]$^+$, M = [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$.

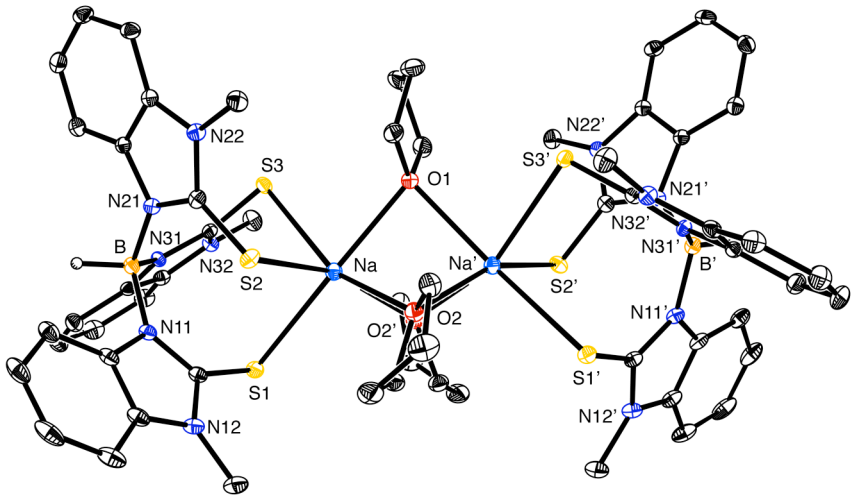


Molecular Structure of [CpCo{P(O)(OEt)$_2$}$_3$]Re(CO)$_3$

Synthesis of [Tm^{MeBenz}]Na

A mixture of 1-methyl-2-benzimidazole-2-thione (300 mg, 1.83 mmol) and $NaBH_4$ (22 mg, 0.58 mmol) was placed in an ampoule and treated with THF (*ca*. 5 mL). The mixture was heated at 160 ˚C for 1 week. After this period, the mixture was filtered and the precipitate was dried *in vacuo* to give {[Tm^{MeBenz}]Na}$_2$(THF)$_3$ as an off-white powder (200 mg, 56%). Analysis calcd. for {[Tm^{MeBenz}]Na}$_2$(THF)$_3$: C, 56.7%; H, 5.9%; N 13.2%. Found: C, 56.6%; H, 5.2%; N 13.5%. ^{1}H NMR for {[Tm^{MeBenz}]Na}$_2$(THF)$_3$ (d_6-DMSO): 1.76 [m, 12H of 3CH_2 of THF], 3.60 [m, 12H of 3CH_2 of THF], 3.64 [s, 18H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CS}$_3$], 6.74 [t, $^3J_{H\text{-}H}$ = 7, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 6.86 [b, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 6.94 [t, $^3J_{H\text{-}H}$ = 8, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 7.19 [d, $^3J_{H\text{-}H}$ = 8, 6H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 25.1 [6 C, CH_2 of the THF], 30.3 [6 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CS}$_3$], 67.0 [6 C, CH_2 of the THF], 107.7 [6 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 112.6 [6 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 120.3 [6 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 121.0 [6 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 133.8 [6 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CS}$_3$], 136.6 [6 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CS}$_3$], 172.8 [6 C, HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$S}$_3$]. FAB-MS: m/z = 525.2 [M+1]$^+$, M = [Tm^{MeBenz}]Na. IR Data (KBr disk, cm^{-1}): 3450 (br), 3052 (w), 2929 (w), 2868 (w), 2423 (w) [ν_{BH}], 1620 (m), 1544

(w), 1484 (s), 1460 (w), 1432 (s), 1344 (s), 1293 (s), 1230 (m), 1190 (m), 1158 (m), 1092 (m), 997 (m), 858 (w), 813 (m), 742 (s), 620 (m), 555 (m), 421 (m).



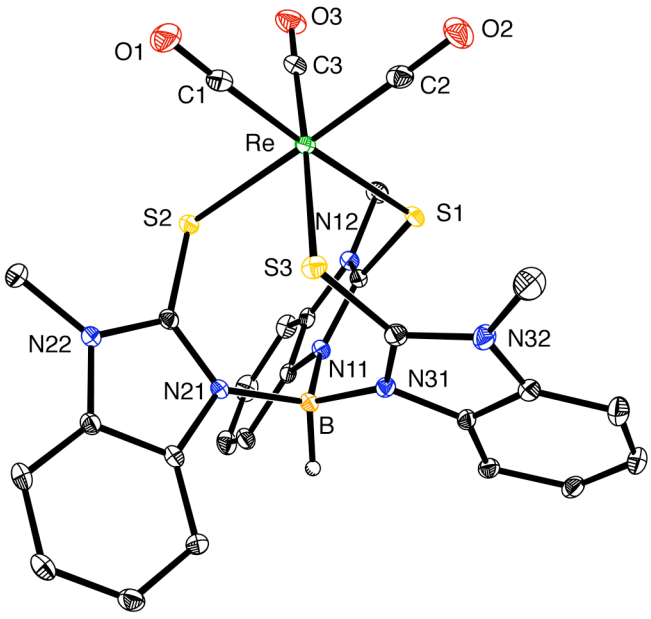
Molecular Structure of {[Tm^{MeBenz}]Na}$_2$(THF)$_3$

[Tm^{MeBenz}]Na free of THF may be obtained by washing with Et_2O. ^{1}H NMR for [Tm^{MeBenz}]Na (d_6-DMSO): 3.64 [s, 9H of HB{(C_4H_4)C_2N_2($C\underline{H}_3$)CS}$_3$], 6.74 [t, $^3J_{H\text{-}H}$ = 7, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 6.87 [b,3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 6.94 [t, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$], 7.18 [d, $^3J_{H\text{-}H}$ = 8, 3H of HB{($C_4\underline{H}_4$)C_2N_2(CH_3)CS}$_3$]. ^{13}C{^{1}H} NMR (d_6-DMSO): 30.3 [3 C, HB{(C_4H_4)C_2N_2($\underline{C}H_3$)CS}$_3$], 107.7 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 112.6 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 120.3 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 121.0 [3 C, HB{($\underline{C}_4H_4$)C_2N_2(CH_3)CS}$_3$], 133.8 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CS}$_3$], 136.6 [3 C, HB{(C_4H_4)$\underline{C}_2N_2$(CH_3)CS}$_3$], 172.8 [3 C, HB{(C_4H_4)C_2N_2(CH_3)$\underline{C}$S}$_3$].

Synthesis of [Tm^{MeBenz}]Re(CO)$_3$

A mixture of [Tm^{MeBenz}]Na•1.5THF (50 mg, 0.08 mmol) and $Re(CO)_5Br$ (33 mg, 0.08 mmol) was placed in an ampoule and treated with THF (*ca.* 5 mL) and heated overnight at 70 °C. The mixture was filtered and the volatile components were removed from the filtrate *in vacuo*. The residue obtained was washed with acetonitrile (*ca.* 5 mL) to give [Tm^{MeBenz}]Re(CO)$_3$ as white powder (20 mg, 33%). Crystals suitable for X-ray diffraction

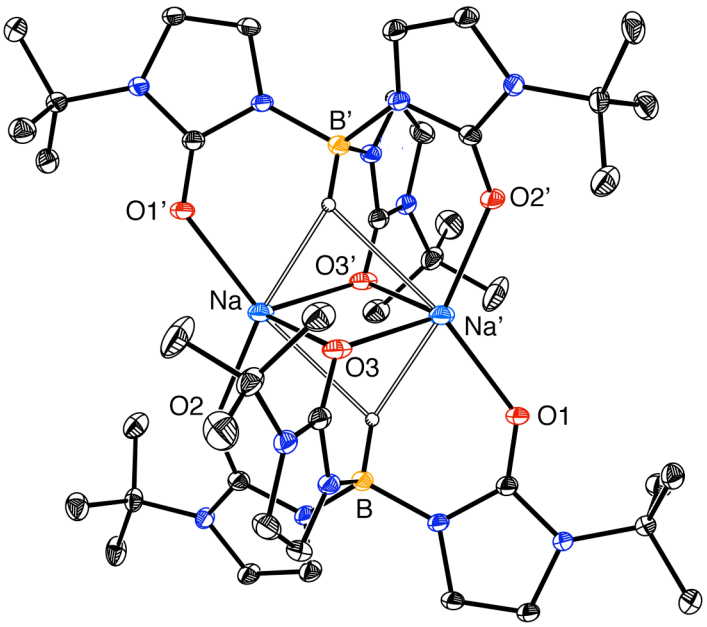
were obtained from slow evaporation from a solution in benzene. Analysis calcd. for $[Tm^{MeBenz}]Re(CO)_3 \cdot 1.8C_6H_6$: C, 49.8%; H, 3.6%; N 9.2%. Found: C, 49.4%; H, 4.6%; N 9.0%. ^1H NMR (C_6D_6): 3.08 [s, 9H of $HB\{(C_4H_4)C_2N_2(C\underline{H}_3)CS\}_3$], 6.54 [d, $^3J_{H\text{-}H} = 8$, 3H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CS\}_3$], 6.96 [m, 6H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CS\}_3$], 7.58 [d, $^3J_{H\text{-}H} = 8$, 3H of $HB\{(C_4\underline{H}_4)C_2N_2(CH_3)CS\}_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 30.6 [3 C, $HB\{(C_4H_4)C_2N_2(\underline{C}H_3)CS\}_3$], 110.8 [3C, $HB\{(\underline{C}_4H_4)C_2N_2(CH_3)CS\}_3$], 113.3 [3C, $HB\{(\underline{C}_4H_4)C_2N_2(CH_3)CS\}_3$], 123.7 [3C, $HB\{(\underline{C}_4H_4)C_2N_2(CH_3)CS\}_3$], 124.1 [3C, $HB\{(\underline{C}_4H_4)C_2N_2(CH_3)CS\}_3$], 133.7 [$HB\{(C_4H_4)\underline{C}_2N_2(CH_3)CS\}_3$], 135.7 [$HB\{(C_4H_4)\underline{C}_2N_2(CH_3)CS\}_3$], 167.5 [$HB\{(C_4H_4)C_2N_2(CH_3)\underline{C}S\}_3$]. FAB-MS: $m/z = 772.1$ $[M]^+$, $M = [Tm^{MeBenz}]Re(CO)_3$. IR Data (KBr disk, cm^{-1}): 2925 (m), 2010 (s) [ν_{CO}], 1922 (s) [ν_{CO}], 1478 (m), 1439 (m), 1409 (m), 1363 (m), 1293 (m), 1233 (w), 1193 (w), 1149 (w), 1120 (w), 1094 (w), 1014 (w), 853 (m), 812 (m), 749 (m), 672 (w), 624 (m), 556 (w), 516 (w), 482 (w), 437 (w), 420 (w). IR Data (CH_2Cl_2, cm^{-1}): 2014 (m) [ν_{CO}], 1895 (m) [ν_{CO}].



Molecular Structure of $[Tm^{MeBenz}]Re(CO)_3$

Synthesis of [To^{But}]Na

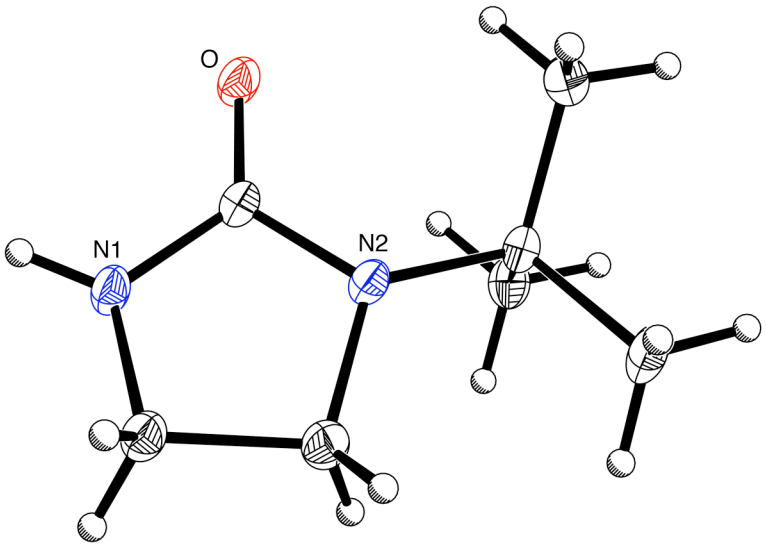
A mixture of 1-*tert*-butyl-1,3-dihydro-2*H*-imidazol-2-one (200 mg, 1.43 mmol) and $NaBH_4$ (18 mg, 0.47 mmol) was placed in an ampoule and treated with THF (4 mL). The mixture was heated at 180 ˚C for 9 days and cooled to room temperature. The volatile components were removed *in vacuo* and the residue obtained was crystallized from pentane (*ca*. 5 mL) and dried to give [To^{But}]Na as colorless crystals (14 mg, 7%). ^{1}H NMR (C_6D_6): 1.37 [s, 27H of HB{$C_2N_2H_2$[C(C$\underline{H}_3$)$_3$]CO}$_3$], 6.08 [d, $^{3}J_{H\text{-}H}$ = 3, 3H of HB{$C_2N_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$], 6.62 [br, 3H of HB{$C_2N_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 28.5 [9 C, HB{$C_2N_2H_2$[C($\underline{C}$H$_3$)$_3$]CO}$_3$], 53.9 [3 C, HB{$C_2N_2H_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_3$], 107.7 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 112.3 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 157.6 [3 C, HB{$C_2N_2H_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_3$]. FAB-MS: *m*/*z* = 475.3 [M + Na]$^{+}$, M = [To^{But}]Na.



Molecular Structure of {[To^{But}]Na}$_2$

The formation of [To^{But}]Na, however, is accompanied side reactions, one of which the C=C double bond of the imidazolone ring is reduced, thereby resulting in the formation of 1-t-butylimidazolidinone, which was identified by ^{1}H NMR spectroscopy and X–ray diffraction. ^{1}H NMR for 1-t-butylimidazolidinone (C_6D_6): 1.29 [s, 9H of

$C_2H_4NHN[C(C\underline{H}_3)_3]CO]$, 2.43 [t, $^3J_{H\text{-}H}$ = 8, 2H of $C_2\underline{H}_4NHN[C(CH_3)_3]CO]$, 2.69 [t, $^3J_{H\text{-}H}$ = 8, 2H of $C_2\underline{H}_4NHN[C(CH_3)_3]CO]$, NH not observed.

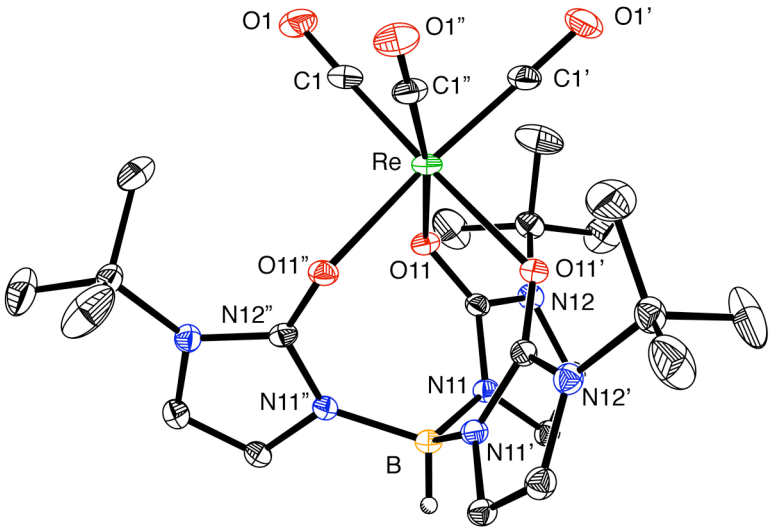


Molecular Structure of 1-t-butylimidazolidinone

Synthesis of [To^{But}]Re(CO)$_3$

A mixture of [To^{But}]Na (14 mg, 0.03 mmol) and $Re(CO)_5Br$ (15 mg, 0.04 mmol) was treated with benzene (*ca.* 1 mL) and heated at 70 ˚C overnight, during which period a small amount of colorless blocks of [To^{But}]Re(CO)$_3$ suitable for X-ray were deposited and isolated by filtration. The filtrate was lyophilized resulting in a white powder. The residue was dissolved in hexane/Et_2O (*ca.* 50:50) to give a solution from which colorless crystals of [To^{But}]Re(CO)$_3$ were obtained by slow evaporation (8 mg, 37%). ^{1}H NMR (C_6D_6): 1.29 [s, 27H of $HB\{C_2N_2H_2[C(C\underline{H}_3)_3]CO\}_3]$, 5.87 [d, $^3J_{H\text{-}H}$ = 3, 3H of $HB\{C_2N_2\underline{H}_2[C(CH_3)_3]CO\}_3]$, 6.28 [d, $^3J_{H\text{-}H}$ = 3, 3H of $HB\{C_2N_2\underline{H}_2[C(CH_3)_3]CO\}_3]$. $^{13}C\{^1H\}$ NMR (C_6D_6): 29.1 [9 C, $HB\{C_2N_2H_2[C(\underline{C}H_3)_3]CO\}_3]$, 55.9 [3 C, $HB\{C_2N_2H_2[\underline{C}(CH_3)_3]CO\}_3]$, 110.4 [3 C, $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CO\}_3]$, 116.8 [3 C, $HB\{\underline{C}_2N_2H_2[C(CH_3)_3]CO\}_3]$, 157.0 [3 C, $HB\{C_2N_2H_2[C(CH_3)_3]\underline{C}O\}_3]$. FAB-MS: m/z = 700.6 $[M]^+$, M = [To^{But}]Re(CO)$_3$ superimposed by $[M+1]^+$; m/z = 672.6 $[M\text{-}CO]^+$, M = [To^{But}]Re(CO)$_3$. IR Data (KBr disk, cm^{-1}): IR Data (KBr disk, cm^{-1}): 2979 (m), 2925 (m), 2431 (w) [ν_{BH}], 2017 (vs) [ν_{CO}], 1879

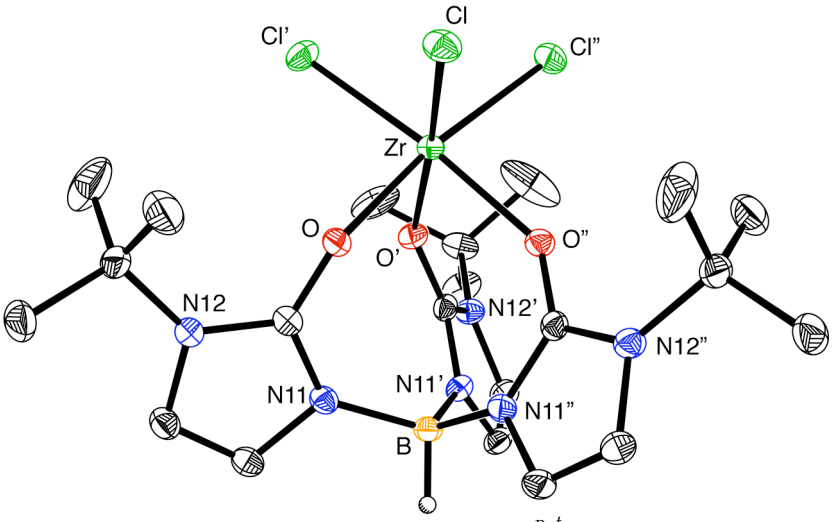
(vs) [ν_{CO}], 1621 (s), 1587 (s), 1436 (m), 1370 (w), 1215 (m), 1194 (m), 1085 (w), 805 (w), 773 (w), 743 (w), 680 (w). IR Data (CH_2Cl_2, cm^{-1}): 2018 (m) [ν_{CO}], 1887 (s) [ν_{CO}].



Molecular Structure of [To^{But}]Re(CO)$_3$

Synthesis of [To^{But}]ZrCl$_3$

A mixture of [To^{But}]Na (16 mg, 0.04 mmol) and $ZrCl_4$ (12.3 mg, 0.05 mmol) was treated with benzene (*ca.* 1 mL) and heated at 60 ˚C for 4 hours, during which period a small amount of colorless blocks of [To^{But}]$ZrCl_3$ suitable for X-ray were deposited. The mixture was filtered and the residue was extracted with chloroform (3 × *ca.* 3 mL). The volatile components were removed *in vacuo* and the residue obtained was washed with hexanes (*ca.* 3 mL) yielding [To^{But}]$ZrCl_3$ as an off-white powder (6 mg, 27%). ^{1}H NMR (C_6D_6): 1.66 [s, 27H of HB{$C_2N_2H_2$[C(C$\underline{H}_3$)$_3$]CO}$_3$], 6.46 [d, $^3J_{H\text{-}H}$ = 3, 3H of HB{$C_2N_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$], 6.50 [d, $^3J_{H\text{-}H}$ = 3, 3H of HB{$C_2N_2\underline{H}_2$[C(CH$_3$)$_3$]CO}$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): 29.4 [9 C, HB{$C_2N_2H_2$[C($\underline{C}$H$_3$)$_3$]CO}$_3$], 57.9 [3 C, HB{$C_2N_2H_2$[$\underline{C}$(CH$_3$)$_3$]CO}$_3$], 110.7 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 119.0 [3 C, HB{$\underline{C}_2N_2H_2$[C(CH$_3$)$_3$]CO}$_3$], 152.7 [3 C, HB{$C_2N_2H_2$[C(CH$_3$)$_3$]$\underline{C}$O}$_3$].



Molecular Structure of $[To^{Bu^t}]ZrCl_3$

Table 1. Crystal, intensity collection and refinement data.

	[To$^{Bu^t}$]Na	**[To$^{Bu^t}$]ZrCl$_3$**
lattice	Triclinic	Trigonal
formula	$C_{42}H_{68}B_2N_{12}Na_2O_6$	$C_{39}H_{52}BCl_3N_6O_3Zr$
formula weight	904.68	861.25
space group	*P-1*	*P-3*
a/Å	10.357(3)	16.242(2)
b/Å	10.900(3)	16.242(2)
c/Å	12.135(4)	9.4661(14)
α/°	104.306(5)	90
β/°	92.511(5)	90
γ/°	108.015(5)	120
V/Å^3	1251.6(6)	2162.6(5)
Z	1	2
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.200	1.323
μ (Mo Kα), mm^{-1}	0.096	0.482
θ max, deg.	26.37	30.50
no. of data collected	15155	35051
no. of data used	5123	4410
no. of parameters	302	111
R_1 [$I > 2\sigma(I)$]	0.0568	0.0436
wR_2 [$I > 2\sigma(I)$]	0.0784	0.1087
R_1 [all data]	0.1517	0.0607
wR_2 [all data]	0.0932	0.1139
GOF	1.092	1.093
R_{int}	0.0880	0.0541

Table 1(cont). Crystal, intensity collection and refinement data.

	[To^{But}]Re(CO)$_3$	**1-t-butyl-imidazolidinone**
lattice	Trigonal	Monoclinic
formula	$C_{42}H_{52}BN_6O_6Re$	$C_7H_{14}N_2O$
formula weight	933.91	142.20
space group	*P-3*	$P2_1/c$
a / Å	16.131(2)	12.2165(13)
b / Å	16.131(2)	6.1075(6)
c / Å	9.6857(14)	10.7386(11)
α / °	90	90
β / °	90	96.338(2)
γ / °	120	90
V / Å^3	2182.6(6)	796.33(14)
Z	2	4
temperature (K)	200(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.421	1.186
μ (Mo Kα), mm^{-1}	2.835	0.081
θ max, deg.	30.71	30.50
no. of data collected	34854	12129
no. of data used	4523	2430
no. of parameters	175	98
R_1 [$I > 2\sigma(I)$]	0.0363	0.0473
wR_2 [$I > 2\sigma(I)$]	0.0586	0.1277
R_1 [all data]	0.0822	0.0655
wR_2 [all data]	0.0714	0.1420
GOF	1.131	1.037
R_{int}	0.0818	0.0431

Table 1(cont). Crystal, intensity collection and refinement data.

	[To^{MeBenz}]Na	**[To^{MeBenz}]ZnI**
lattice	Triclinic	Triclinic
formula	$C_{30}H_{36}BN_6NaO_6$	$C_{25.5}H_{25}BCl_3IN_6O_3Zn$
formula weight	610.45	772.95
space group	*P-1*	*P-1*
a / Å	13.7551(9)	9.361(5)
b / Å	14.9081(10)	11.221(7)
c / Å	15.2676(10)	17.165(13)
α / °	82.3230(10)	96.785(11)
β / °	89.7710(10)	103.212(11)
γ / °	81.6210(10)	113.522(8)
V / Å^3	3069.2(4)	1564.5(18)
Z	4	2
temperature (K)	200(2)	200(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.321	1.641
μ (Mo Kα), mm^{-1}	0.105	2.065
θ max, deg.	32.57	30.15
no. of data collected	52297	24328
no. of data used	20703	9138
no. of parameters	811	368
R_1 [$I > 2\sigma(I)$]	0.0494	0.0520
wR_2 [$I > 2\sigma(I)$]	0.1178	0.1122
R_1 [all data]	0.1003	0.1108
wR_2 [all data]	0.1427	0.1336
GOF	1.021	1.009
R_{int}	0.0373	0.0531

Table 1(cont). Crystal, intensity collection and refinement data.

	$[To^{MeBenz}]_2Co$	$[To^{MeBenz}]_2Fe$
lattice	Triclinic	Triclinic
formula	$C_{50}H_{46}B_2Cl_6CoN_{12}O_6$	$C_{50}H_{46}B_2Cl_6FeN_{12}O_6$
formula weight	1204.24	1201.16
space group	*P-1*	*P-1*
a / Å	11.027(2)	9.765(7)
b / Å	11.171(2)	11.496(8)
c / Å	11.536(2)	13.698(9)
α / °	85.955(3)	87.906(10)
β / °	78.386(3)	69.479(10)
γ / °	74.761(3)	72.277(10)
V / Å^3	1342.8(4)	1367.6(16)
Z	1	1
temperature (K)	160(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.489	1.458
μ (Mo Kα), mm^{-1}	0.680	0.629
θ max, deg.	30.47	30.62
no. of data collected	21660	16628
no. of data used	8101	8255
no. of parameters	356	356
R_1 [$I > 2\sigma(I)$]	0.0637	0.0670
wR_2 [$I > 2\sigma(I)$]	0.1400	0.1219
R_1 [all data]	0.1520	0.1569
wR_2 [all data]	0.1701	0.1527
GOF	1.000	1.000
R_{int}	0.0761	0.0727

Table 1(cont). Crystal, intensity collection and refinement data.

	$[To^{MeBenz}]Re(CO)_3$	$[To^{MeBenz}]ZrCl_3$
lattice	Rhombohedral	Monoclinic
formula	$C_{27}H_{22}BN_6O_6Re$	$C_{25}H_{23}BCl_6N_6O_3Zr$
formula weight	723.52	770.22
space group	*R-3*	$P2_1/n$
a / Å	15.5893(14)	15.611(3)
b / Å	15.5893(14)	12.966(3)
c / Å	19.0929(14)	15.764(4)
α / °	90	90
β / °	90	103.384(4)
γ / °	120	90
V / Å^3	4018.4(6)	3104.4(12)
Z	6	4
temperature (K)	123(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.794	1.648
μ (Mo Kα), mm^{-1}	4.590	0.910
θ max, deg.	32.71	26.37
no. of data collected	23365	36423
no. of data used	3200	6363
no. of parameters	127	385
R_1 [$I > 2\sigma(I)$]	0.0167	0.0544
wR_2 [$I > 2\sigma(I)$]	0.0410	0.0837
R_1 [all data]	0.0187	0.1321
wR_2 [all data]	0.0418	0.1052
GOF	1.063	1.002
R_{int}	0.0271	0.1740

Table 1(cont). Crystal, intensity collection and refinement data.

	$Cp[To^{MeBenz}]ZrCl_2$	**$[CpCo\{P(O)(OEt)_2\}_3]$-$Re(CO)_3$**
lattice	Triclinic	Monoclinic
formula	$C_{35}H_{33}BCl_2N_6O_3Zr$	$C_{20}H_{35}CoO_{12}P_3Re$
formula weight	758.60	805.52
space group	*P-1*	$P2_1/n$
a / Å	10.0122(17)	11.4131(7)
b / Å	12.326(2)	18.4005(11)
c / Å	15.991(3)	13.6761(8)
α / °	69.229(2)	90
β / °	72.820(2)	92.8560(10)
γ / °	71.988(2)	90
V / Å^3	1716.0(5)	2868.5(3)
Z	2	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.468	1.865
μ (Mo Kα), mm^{-1}	0.521	5.018
θ max, deg.	30.61	32.48
no. of data collected	28027	48946
no. of data used	10491	10043
no. of parameters	439	341
R_1 [$I > 2\sigma(I)$]	0.0483	0.0355
wR_2 [$I > 2\sigma(I)$]	0.0798	0.0601
R_1 [all data]	0.0939	0.0694
wR_2 [all data]	0.0922	0.0686
GOF	1.002	1.001
R_{int}	0.0722	0.0705

Table 1(cont). Crystal, intensity collection and refinement data.

	[Tm^{MeBenz}]Na	**[Tm^{MeBenz}]Re(CO)$_3$**
lattice	Monoclinic	Monoclinic
formula	$C_{60}H_{68}B_2N_{12}Na_2O_3S_6$	$C_{33}H_{28}BN_6O_3ReS_3$
formula weight	1265.22	849.80
space group	*C2/c*	$P2_1/c$
a / Å	34.381(13)	16.147(3)
b / Å	16.553(6)	10.510(2)
c / Å	11.073(4)	19.719(4)
α / °	90	90
β / °	96.783(6)	93.087(3)
γ / °	90	90
V / Å^3	6257(4)	3341.5(12)
Z	4	4
temperature (K)	125(2)	125(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.343	1.689
μ (Mo Kα), mm^{-1}	0.288	3.868
θ max, deg.	30.55	32.75
no. of data collected	37010	56925
no. of data used	9564	11778
no. of parameters	392	431
R_1 [$I > 2\sigma(I)$]	0.0482	0.0311
wR_2 [$I > 2\sigma(I)$]	0.0990	0.0577
R_1 [all data]	0.1018	0.0516
wR_2 [all data]	0.1176	0.0635
GOF	1.012	1.000
R_{int}	0.0796	0.0557

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