SUPPORTING INFORMATION

Synthesis and Structural Characterization of *Tris*(2-pyridonyl)methyl Complexes of Zinc and Thallium: A New Class of Metallacarbatranes and a Monovalent Thallium Alkyl Compound

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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.[1] Solvents were purified and degassed by standard procedures. ^{1}H NMR spectra were measured on Bruker 300 DRX, Bruker 400 DRX, Bruker 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 $CHCl_3$, 5.32 for $CDHCl_2$ 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 128.06 for C_6D_6, 53.84 for CD_2Cl_2, 77.16 for $CDCl_3$, and 39.52 for d_6-DMSO).[2] Coupling constants are given in hertz. Infrared spectra were recorded on PerkinElmer Spectrum Two 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. All chemicals were obtained from Aldrich and $Zn[N(SiMe_3)_2]_2$[3] and $TlN(SiMe_3)_2$[4] were obtained by the literature methods.

X-ray structure determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and 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 2008/4).[5]

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.7 (release 107) suite of *ab initio* quantum chemistry programs.[6] Geometry optimizations were performed with the B3LYP density functional[7] using the 6-31G** (C, H, N, O) and LAV3P (Tl) basis sets.[8] NBO calculations were performed with NBO 5.0[9] as implemented in the Jaguar 7.7 (release 107) suite of programs using the 6-31G** and LAV3P basis sets. Molecular orbital analyses were performed with the aid of JIMP2,[10] which employs Fenske-Hall calculations and visualization using MOPLOT.[11]

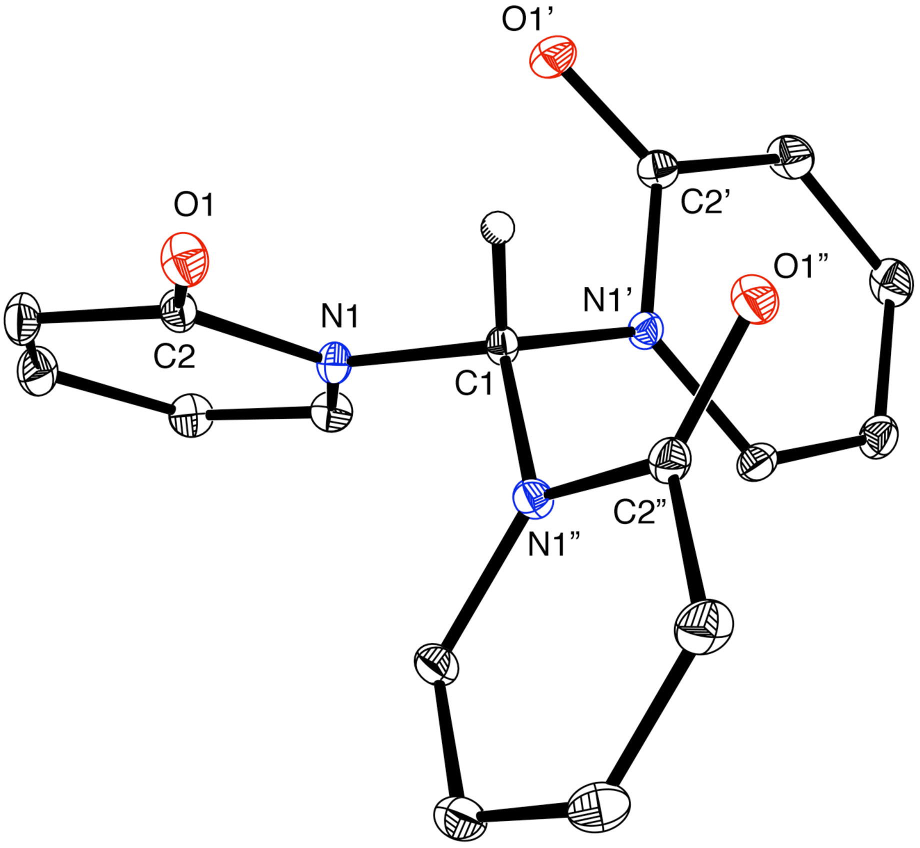
Synthesis of $HC(NC_5H_4O)_3$, [Tpom]H

(a) A triphasic mixture of 2-pyridone (9.0 g, 94.6 mmol), [$Bu^n{}_4N$]Br (0.6 g, 1.86 mmol) and K_2CO_3 (40 g, 289 mmol) in $CHCl_3$ (90 mL) and water (90 mL) was refluxed for 6 days. The mixture was allowed to cool to room temperature and was treated with water (*ca.* 500 mL) and CH_2Cl_2 (*ca.* 600 mL), resulting in the formation of two layers. The organic layer was separated, dried over Na_2SO_4 and filtered. The volatile components were removed *in vacuo* to give a dark brown residue that was subjected to column chromatography on silica gel. Elution with a mixture of ethylacetate and hexane (1:1 with 1% v/v Et_3N) produced $HC(OC_5H_4N)_3$ (600 mg, 6 %), while elution with a mixture of ethylacetate and hexane (2:1 with 1% v/v Et_3N) yielded $HC(OC_5H_4N)_2(NC_5H_4O)$ (750 mg, 8 %). Analysis calcd. for $HC(OC_5H_4N)_3$: C, 65.1%; H, 4.4%; N 14.2% Found: C, 65.2%; H, 3.8%; N 14.2%. ^{1}H NMR ($CDCl_3$): 6.86 [d, $^3J_{H-H}$ = 8, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 6.94 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 7.61 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 8.14 [m, 3H of $CH\{(OC)N(C_4\underline{H}_4)\}_3$], 9.28 [s, 1H of $C\underline{H}\{(OC)N(C_4H_4)\}_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 104.0 [1C of $\underline{C}H\{(OC)N(C_4H_4)\}_3$], 111.5 [3C of $CH\{(OC)N(\underline{C}_4H_4)(CO)\}_3$], 118.6 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 139.2 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 147.3 [3C of $CH\{(OC)N(\underline{C}_4H_4)\}_3$], 161.2 [3C of $CH\{(O\underline{C})N(C_4H_4)\}_3$]. FAB-MS: *m/z* = 296.16 $[M+1]^+$, M = $HC(OC_5H_4N)_3$. IR Data (ATR, cm^{-1}): 3015 (w), 2963 (w), 1658 (br), 1594 (s), 1573 (s), 1541 (w), 1468 (s), 1431 (s), 1356 (w), 1340 (w), 1284 (w), 1259 (s), 1231 (s), 1143 (w), 1102 (m), 1049 (vs), 1021 (vs), 990 (vs), 914 (m), 854 (m), 772 (vs), 735 (m), 664 (w), 615 (w), 559 (w), 513 (m), 496 (m). Analysis calcd. for $HC(OC_5H_4N)_2(NC_5H_4O)$: C, 65.1%; H, 4.4%; N 14.2% Found: C, 65.4%; H, 3.9%; N 14.2%. ^{1}H NMR ($CDCl_3$): 6.20 ["dt", $^3J_{H-H}$ = 7, $^4J_{H-H}$ = 1, 1H of

$\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}]$, 6.58 [d, $^3J_{H\text{-}H} = 9$, 1H of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}]$, 6.86 [d, $^3J_{H\text{-}H} = 8$, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 6.96 [m, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 7.31 [m, 1H of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}]$, 7.63 [m, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 7.79 [dd, $^3J_{H\text{-}H} = 7$, $^3J_{H\text{-}H} = 2$, 1H of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4\underline{H}_4)(CO)\}]$, 8.15 [m, 2H of $\{(C_4\underline{H}_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 9.31 [s, 1H of $\{(C_4H_4)N(CO)\}_2C\underline{H}\{N(C_4H_4)(CO)\}]$. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 93.1 [1C of $\{(C_4H_4)N(CO)\}_2\underline{C}H\{N(C_4H_4)(CO)\}]$, 106.2 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}]$, 111.0 [2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 119.0 [2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 121.7 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}]$, 132.1 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}]$, 139.4 [2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 139.9 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(\underline{C}_4H_4)(CO)\}]$, 147.6 [2C of $\{(\underline{C}_4H_4)N(CO)\}_2CH\{N(C_4H_4)(CO)\}]$, 160.7 [2C of $\{(C_4H_4)N(\underline{C}O)\}_2CH\{N(C_4H_4)(CO)\}]$, 161.6 [1C of $\{(C_4H_4)N(CO)\}_2CH\{N(C_4H_4)(\underline{C}O)\}]$. FAB-MS: $m/z = 296.2$ $[M+1]^+$, M = $HC(OC_5H_4N)_2(NC_5H_4O)$. IR Data (ATR, cm^{-1}): 3065 (w), 2963 (w), 1670 (s), 1595 (s), 1574 (m), 1537 (m), 1471 (s), 1432 (s), 1401 (w), 1364 (w), 1342 (w), 1292 (w), 1261 (m), 1226 (s), 1187 (w), 1176 (m), 1142 (m), 1117 (s), 1102 (s), 1067 (s), 1047 (s), 1020 (vs), 918 (s), 881 (m), 788 (s), 762 (vs), 672 (w), 647 (w), 630 (w), 618 (w), 603 (w), 575 (w), 557 (w), 513 (m), 494 (m).

(b) A mixture of $HC(OC_5H_4N)_3$ (392 mg, 1.33 mmol) and camphorsulfonic acid (40 mg, 0.17 mmol) in anhydrous toluene (*ca.* 2 mL) and THF (*ca.* 2 mL) was heated at 180 ˚C in a sealed tube for 5 days. The mixture was allowed to cool to room temperature, thereby depositing a brown precipitate. The mixture was filtered and the precipitate was washed with Et_2O (*ca.* 5 mL) and acetone (*ca.* 5 mL) and dried *in vacuo* to give $HC(NC_5H_4O)_3$ as a brown powder (110 mg, 28 %). Analysis calcd. for $HC(NC_5H_4O)_3$: C, 65.1%; H, 4.4%; N 14.2% Found: C, 65.1%; H, 3.8%; N 14.0%. ^1H NMR (DMSO): 6.39 ["dt", $^3J_{H\text{-}H} = 7$, $^4J_{H\text{-}H} = 1$, 3H of $CH\{N(C_4\underline{H}_4)(CO)\}_3]$, 6.52 [d, $^3J_{H\text{-}H} = 9$, 3H of $CH\{N(C_4\underline{H}_4)(CO)\}_3]$, 7.22 [dd, $^3J_{H\text{-}H} = 7$, $^4J_{H\text{-}H} = 1$, 3H of $CH\{N(C_4\underline{H}_4)(CO)\}_3]$, 7.57 [m, 3H of

$CH\{N(C_4\underline{H}_4)(CO)\}_3]$, 8.53 [s, 1H of $C\underline{H}\{N(C_4H_4)(CO)\}_3]$. $^{13}C\{^1H\}$ NMR (DMSO): 74.0 [1C of $\underline{C}H\{N(C_4H_4)(CO)\}_3]$, 107.0 [3C of $CH\{N(\underline{C}_4H_4)(CO)\}_3]$, 120.4 [3C of $CH\{N(\underline{C}_4H_4)(CO)\}_3]$, 133.4 [3C of $CH\{N(\underline{C}_4H_4)(CO)\}_3]$, 141.3 [3C of $CH\{N(\underline{C}_4H_4)(CO)\}_3]$, 160.4 [3C of $CH\{N(C_4H_4)(\underline{C}O)\}_3]$. FAB-MS: $m/z = 296.2$ $[M+1]^+$, M = $HC(NC_5H_4O)_3$. IR Data (ATR, cm^{-1}): 3088 (w), 3034 (w), 1654 (vs), 1582 (vs), 1531 (vs), 1469 (w), 1458 (w), 1433 (w), 1399 (w), 1356 (w), 1304 (w), 1243 (s), 1182 (m), 1145 (m), 1133 (m), 1115 (m), 1094 (w), 1053 (w), 1019 (w), 994 (w), 952 (w), 903 (m), 852 (w), 807 (w), 764 (vs), 729 (m), 610 (w), 565 (m), 530 (m), 508 (s). Brown needle-shaped crystals of $HC(NC_5H_4O)_3$ suitable for X-ray were obtained from the reaction mixture.

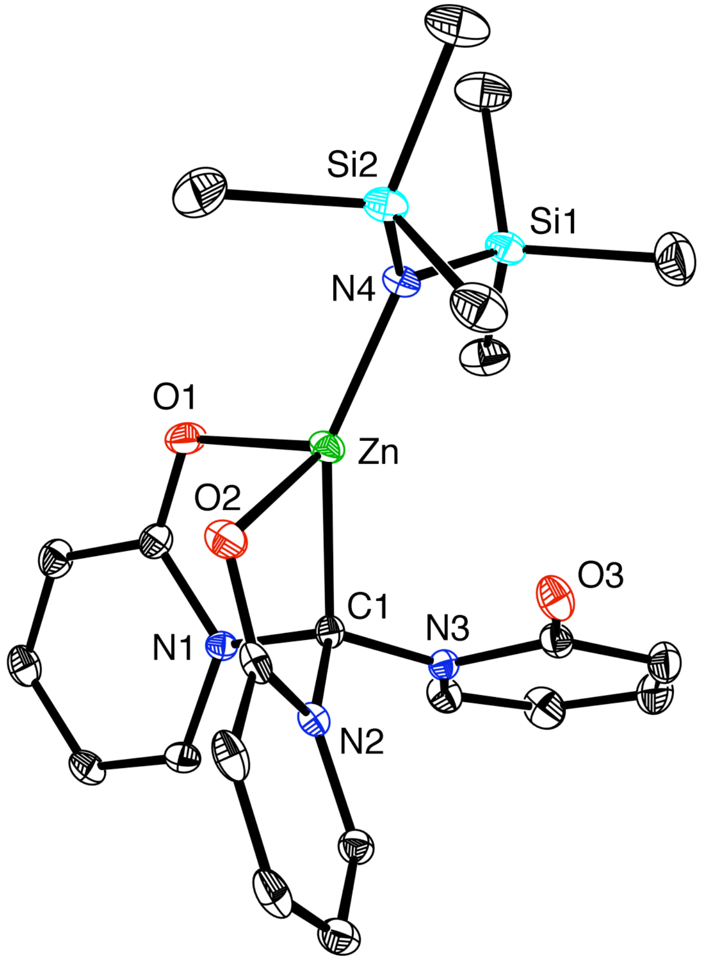


Molecular Structure of [Tpom]H

Synthesis of [κ^3-Tpom]ZnN(SiMe$_3$)$_2$

A mixture of [Tpom]H (18.0 mg, 0.06 mmol) and $Zn[N(SiMe_3)_2]_2$ (20.0 mg, 0.05 mmol) in C_6D_6 (*ca.* 2 mL) was heated for 3 weeks at 130 ˚C in an NMR tube equipped with a J.

Young valve. The mixture was lyophilized and the residue obtained was extracted with Et_2O (*ca.* 2 mL). The extract was cooled to -15 ˚C, thereby depositing colorless crystals of [κ^3-Tpom]ZnN(SiMe$_3$)$_2$, suitable for X-ray diffraction (10.0 mg, 32%). ^{1}H NMR (C_6D_6): 0.58 [s, 18H of $\{(C\underline{H}_3)_3Si\}_2NZnC\{N(C_4H_4)(CO)\}_3$], 5.45 [“dt”, $^3J_{H\text{-}H} = 7$, $^4J_{H\text{-}H} = 2$, 3H of $\{(CH_3)_3Si\}_2NZnC\{N(C_4H_4)(CO)\}_3$], 6.38 [m, 3H of $\{(CH_3)_3Si\}_2NZnC\{N(C_4\underline{H}_4)(CO)\}_3$], 6.48 [m, 3H of $\{(CH_3)_3Si\}_2NZnC\{N(C_4\underline{H}_4)(CO)\}_3$], 6.55 [m, 3H of $\{(CH_3)_3Si\}_2NZnC\{N(C_4\underline{H}_4)(CO)\}_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 5.8 [6C of $\{(\underline{C}H_3)_3Si\}_2NZnC\{N(C_4H_4)(CO)\}_3$], 75.2 [1C of $\{(CH_3)_3Si\}_2NZn\underline{C}\{N(C_4H_4)(CO)\}_3$], 108.1 [3C of $\{(CH_3)_3Si\}_2NZnC\{N(\underline{C}_4H_4)(CO)\}_3$], 120.8 [3C of $\{(CH_3)_3Si\}_2NZnC\{N(\underline{C}_4H_4)(CO)\}_3$], 133.0 [3C of $\{(CH_3)_3Si\}_2NZnC\{N(\underline{C}_4H_4)(CO)\}_3$], 139.2 [3C of $\{(CH_3)_3Si\}_2NZnC\{N(\underline{C}_4H_4)(CO)\}_3$], 164.2 [3C of $\{(CH_3)_3Si\}_2NZnC\{N(C_4H_4)(\underline{C}O)\}_3$].



Molecular Structure of [κ^3-Tpom]ZnN(SiMe$_3$)$_2$

Synthesis of 4-tert-butylpyridine-*N*-oxide

4-tert-butylpyridine-*N*-oxide was prepared by a modification of the literature method.[12] Hydrogen peroxide (40 mL, 35% in water) was added to a mixture of 4-tert-butylpyridine (18.5 g, 137 mmol) and glacial acetic acid (200 mL) and the mixture was heated for 4 hours at 100 ˚C under an atmosphere of N_2. The mixture was allowed to cool to room temperature, treated with another aliquot of hydrogen peroxide (40 mL, 35%) and heated for 4 hours at 100 ˚C. The mixture was allowed to cool to room temperature, concentrated *in vacuo* to a volume of *ca.* 100 mL and neutralized with NaOH (1 M). The mixture was extracted into CH_2Cl_2 (*ca.* 700 mL) and the organic layer was collected and dried over Na_2SO_4, after which the volatile components were removed *in vacuo* to yield a yellow solid which was washed with pentane (*ca.* 50 mL) to yield 4-tert-butylpyridine-*N*-oxide (16.5 g, 80 %).

Synthesis of 4-tert-butyl-2-[1*H*]-pyridone

4-*tert*-Butyl-2-[1*H*]-pyridone was prepared by modification of a literature method.[13] A mixture of 4-tert-butylpyridine-*N*-oxide (10.7 g, 70.8 mmol) and acetic anhydride (30 mL) was refluxed for 16 hours under an atmosphere of nitrogen. The mixture was allowed to cool to room temperature and concentrated *in vacuo* to a volume of *ca.* 15 mL and poured into ice water (600 mL). $NaHCO_3$ was added until the solution became alkaline (pH = 8 - 9) and the resulting mixture was stirred for *ca*. 3 days and then extracted with ethylacetate (700 mL). The organic layer was collected and dried over Na_2SO_4, after which the volatile components were removed *in vacuo* to give 4-tert-butyl-2-[*1H*]-pyridone as a brown powder (5.9 g, 55 %). Analysis calcd. for 4-tert-butyl-2-[*1H*]-pyridone: C, 71.5%; H, 8.7%; N 9.3% Found: C, 71.5%; H, 8.3%; N 9.0%. ^1H NMR (C_6D_6): 0.92 [s, 9H of $HN(C_3H_3)(CC(C\underline{H}_3)_3)(CO)$], 5.70 [dd, $^3J_{H\text{-}H} = 7$, $^4J_{H\text{-}H} = 1$, 1H of $HN(C_3\underline{H}_3)(CC(CH_3)_3)(CO)$], 6.68 [br, 1H of $HN(C_3\underline{H}_3)(CC(CH_3)_3)(CO)$], 6.88 [d, $^3J_{H\text{-}H} = 7$, 1H of $HN(C_3\underline{H}_3)(CC(CH_3)_3)CO)$], not showing [1H of $\underline{H}N(C_3H_3)(CC(CH_3)_3)(CO)$]. $^{13}C\{^1H\}$

NMR (C_6D_6): 29.6 [3C of $HN(C_3H_3)(CC(\underline{C}H_3)_3)(CO)$], 34.8 [1C of $HN(C_3H_3)(C\underline{C}(CH_3)_3)(CO)$], 105.3 [1C of $HN(\underline{C}_3H_3)(CC(CH_3)_3)(CO)$], 115.7 [1C of $HN(\underline{C}_3H_3)(CC(CH_3)_3)(CO)$], 134.1 [1C of $HN(\underline{C}_3H_3)(CC(CH_3)_3)(CO)$], 165.0 [1C of $HN(C_3H_3)(\underline{C}C(CH_3)_3)(CO)$], 166.5 [1C of $HN(C_3H_3)(CC(CH_3)_3)(\underline{C}O)$]. MS: *m*/*z* = 151.2 $[M]^+$, M = $HNC_5H_3Bu^tO$. IR Data (ATR, cm^{-1}): 2961 (m), 2868 (w), 1648 (s), 1605 (vs), 1553 (m), 1480 (m), 1459 (m), 1406 (s), 1364 (w), 1344 (w), 1330 (w), 1286 (s), 1259 (m), 1218 (m), 1201 (m), 1090 (m), 1038 (vs), 1022 (vs), 989 (vs), 938 (m), 858 (m), 836 (m), 789 (s), 739 (w), 708 (w), 657 (w), 573 (m), 541 (m), 519 (m), 470 (m).

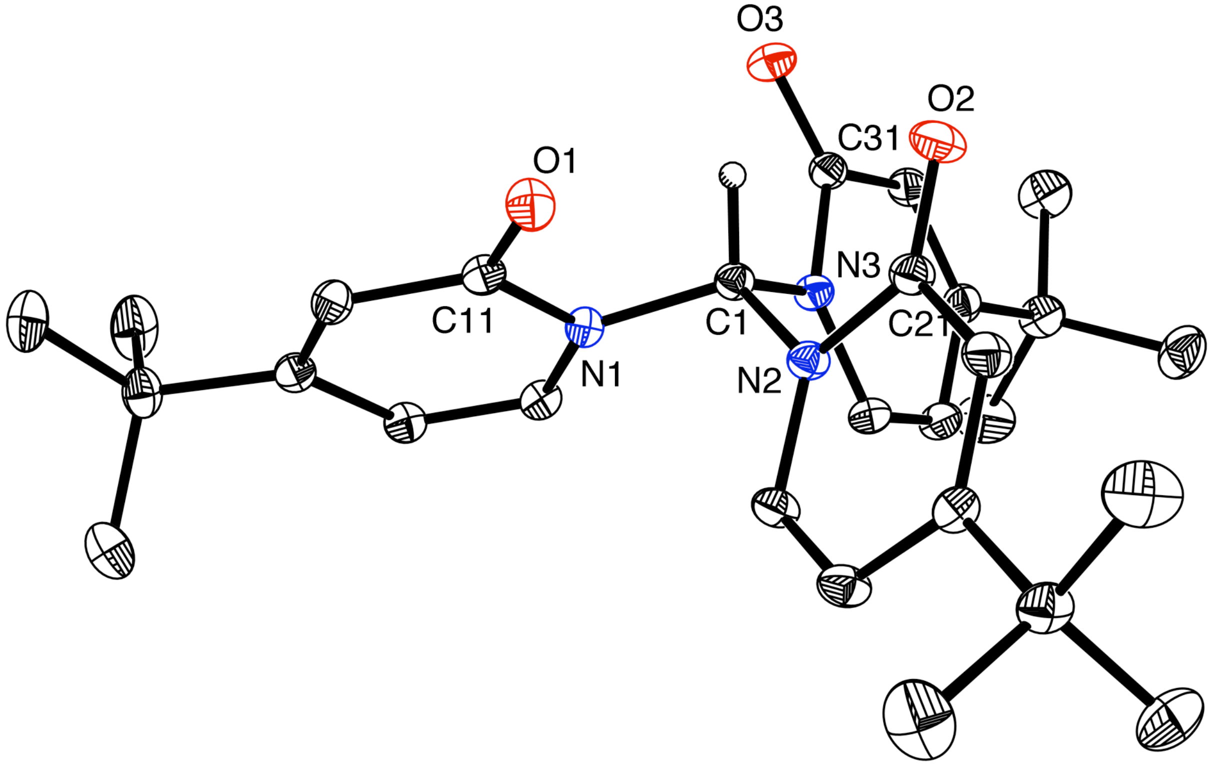
Synthesis of $HC(NC_5H_3Bu^tO)_3$, $[Tpom^{Bu^t}]H$

(a) A triphasic mixture of 4-tert-butylpyridone (5.8 g, 38.4 mmol), $[Bu^n{}_4N]Br$ (0.5 g, 1.55 mmol) and K_2CO_3 (25 g, 180.9 mmol) in $CHBr_3$ (40 mL) and water (150 mL) was heated at 110 ˚C for 5 days. The mixture was allowed to cool to room temperature and treated with water (400 mL) and CH_2Cl_2 (700 mL). The organic layer was separated and dried over Na_2SO_4, after which the solvent was removed *in vacuo* to give a dark brown residue that was subjected to column chromatography on silica gel. Elution with a mixture of ethylacetate and hexane (1:4 with 2% v/v Et_3N) gave $HC(OC_5H_3Bu^tN)_3$ (1.6 g, 27 %), while elution with a mixture of ethylacetate and hexane (2:3 with 2% v/v Et_3N) yielded $HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$ (600 mg, 10 %). Analysis calcd. for $HC(OC_5H_3Bu^tN)_3$: C, 72.5%; H, 8.0%; N 9.1% Found: C, 72.2%; H, 8.0%; N 9.0%. ^1H NMR ($CDCl_3$): 1.26 [s, 27H of $CH\{(OC)N(C_3H_3)(CC(C\underline{H}_3)_3)\}_3$], 6.86 [d, $^4J_{H\text{-}H} = 1$, 3H of $CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$], 6.95 [dd, $^3J_{H\text{-}H} = 5$, $^4J_{H\text{-}H} = 2$, 3H of $CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$], 8.07 [d, $^3J_{H\text{-}H} = 5$, 3H of $CH\{(OC)N(C_3\underline{H}_3)(CC(CH_3)_3)\}_3$], 9.32 [s, 1H of $C\underline{H}\{(OC)N(C_3H_3)(CC(CH_3)_3)\}_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 30.6 [9C of $CH\{(OC)N(C_3H_3)(CC(\underline{C}H_3)_3)\}_3$], 34.9 [3C of $CH\{(OC)N(C_3H_3)(C\underline{C}(CH_3)_3)\}_3$], 103.9 [1C of $\underline{C}H\{(OC)N(C_3H_3)(CC(CH_3)_3)\}_3$], 108.2 [3C of $CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 116.2 [3C of $CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 147.0 [3C of $CH\{(OC)N(\underline{C}_3H_3)(CC(CH_3)_3)\}_3$], 161.6 [3C of $CH\{(O\underline{C})N(C_3H_3)(CC(CH_3)_3)\}_3$], 163.7 [3C of $CH\{(OC)N(C_3H_3)(\underline{C}C(CH_3)_3)\}_3$]. FAB-MS: *m*/*z* = 464.3 $[M+1]^+$, M = $HC(OC_5H_3Bu^tN)_3$. IR

Data (ATR, cm^{-1}): 2967 (m), 2869 (w), 1604 (s), 1552 (m), 1481 (w), 1460 (w), 1406 (s), 1365 (w), 1343 (w), 1285 (s), 1262 (w), 1218 (m), 1199 (m), 1098 (w), 1036 (vs), 920 (m), 869 (m), 853 (m), 800 (m), 743 (w), 727 (w), 657 (m), 546 (w), 531 (m), 482 (w). Analysis calcd. for $HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$: C, 72.5%; H, 8.0%; N 9.1% Found: C, 71.8%; H, 8.1%; N 9.0%. ^{1}H NMR ($CDCl_3$): 1.22 [s, 9H of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(C\underline{H}_3)_3)(CO)\}$], 1.26 [s, 18H of $\{(CC(C\underline{H}_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 6.26 [dd, $^3J_{H\text{-}H} = 7$, $^4J_{H\text{-}H} = 2$, 1H of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}$], 6.50 [d, $^4J_{H\text{-}H} = 2$, 1H of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}$], 6.84 [d, $^4J_{H\text{-}H} = 1$, 2H of $\{(CC(CH_3)_3)(C_3\underline{H}_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 6.96 [dd, $^3J_{H\text{-}H} = 5$, $^4J_{H\text{-}H} = 2$, 2H of $\{(CC(CH_3)_3)(C_3\underline{H}_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 7.72 [d, $^3J_{H\text{-}H} = 8$, 1H of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}$], 8.06 [d, $^3J_{H\text{-}H} = 5$, 2H of $\{(CC(CH_3)_3)(C_3\underline{H}_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 9.29 [s, 1H of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2C\underline{H}\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$]. ^{13}C{^{1}H} NMR ($CDCl_3$): 29.7 [3C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(\underline{C}H_3)_3)(CO)\}$], 30.6 [6C of $\{(CC(\underline{C}H_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 35.0 [2C of $\{(C\underline{C}(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 35.1 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(C\underline{C}(CH_3)_3)(CO)\}$], 93.0 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2\underline{C}H\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 105.7 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}$], 107.6[2C of $\{(CC(CH_3)_3)(\underline{C}_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 116.3 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}$], 116.6 [2C of $\{(CC(CH_3)_3)(\underline{C}_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 130.8 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}$], 147.2 [2C of $\{(CC(CH_3)_3)(\underline{C}_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 161.2 [2C of $\{(CC(CH_3)_3)(C_3H_3)N(\underline{C}O)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}$], 162.0 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(\underline{C}O)\}$], 163.5 [1C of $\{(CC(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(\underline{C}C(CH_3)_3)(CO)\}$], 163.9 [1C of

$\{(\underline{C}C(CH_3)_3)(C_3H_3)N(CO)\}_2CH\{N(C_3H_3)(CC(CH_3)_3)(CO)\}]$. FAB-MS: *m/z* = 464.3 $[M+1]^+$, M = $HC(OC_5H_3Bu^tN)_2(NC_5H_3Bu^tO)$. IR Data (ATR, cm^{-1}): 2962 (m), 2869 (w), 1669 (s), 1605 (s), 1554 (m), 1532 (w), 1482 (m), 1407 (s), 1365 (w), 1343 (w), 1289 (m), 1258 (s), 1221 (m), 1196 (m), 1133 (m), 1077 (vs), 1016 (vs), 945 (m), 932 (m), 863 (m), 830 (m), 796 (s), 742 (w), 717 (w), 686 (m), 664 (m), 628 (m), 572 (m), 526 (m), 481 (m).

(b) A mixture of $HC(OC_5H_3Bu^tN)_3$ (800 mg, 1.73 mmol) and camphorsulfonic acid (85 mg, 0.37 mmol) in anhydrous toluene (*ca*. 5 mL) and THF (*ca*. 2 mL) was heated at 178 °C for 5 days. After this period, the mixture was allowed to cool to room temperature thereby resulting in the formation of an off-white precipitate. The mixture was filtered and the precipitate was washed with Et_2O (2 × 3 mL) and dried *in vacuo* to yield $HC(NC_5H_3Bu^tO)_3$, $[Tpom^{Bu^t}]$, as an off-white powder (300 mg, 38%). Analysis calcd. for $HC(NC_5H_3Bu^tO)_3$: C, 72.5%; H, 8.0%; N 9.1% Found: C, 71.7%; H, 7.8%; N 8.8%. ^1H NMR ($CDCl_3$): 1.22 [s, 27H of $CH\{N(C_3H_3)(CC(C\underline{H}_3)_3)(CO)\}_3$], 6.26 [dd, $^3J_{H\text{-}H} = 8$, $^4J_{H\text{-}H} = 2$, 3H of $CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3$], 6.46 [d, $^4J_{H\text{-}H} = 2$, 3H of $CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3$], 7.40 [d, $^3J_{H\text{-}H} = 8$, 3H of $CH\{N(C_3\underline{H}_3)(CC(CH_3)_3)CO)\}_3$], 8.37 [s, 1H of $C\underline{H}\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 29.6 [9C of $CH\{N(C_3H_3)(CC(\underline{C}H_3)_3)(CO)\}_3$], 35.2 [3C of $CH\{N(C_3H_3)(C\underline{C}(CH_3)_3)(CO)\}_3$], 79.1 [1C of $\underline{C}H\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3$], 105.8 [3C of $CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3$], 116.3 [3C of $CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3$], 134.4 [3C of $CH\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3$], 162.4 [3C of $CH\{N(C_3H_3)(\underline{C}C(CH_3)_3)(CO)\}_3$], 164.6 [3C of $CH\{N(C_3H_3)(CC(CH_3)_3)(\underline{C}O)\}_3$]. MS: *m/z* = 464.3 $[M+1]^+$, M = $HC(NC_5H_3Bu^tO)_3$. IR Data (ATR, cm^{-1}): 3089 (w), 2967 (m), 2869 (w), 1666 (vs), 1597 (s), 1530 (m), 1475 (m), 1388 (m), 1368 (w), 1317 (w), 1249 (s), 1193 (s), 1118 (m), 1074 (m), 1023 (m), 955 (s), 885 (w), 858 (m), 796 (m), 779 (s), 743 (w), 688 (s), 621 (w), 603 (w), 568 (m), 552 (m), 526 (m), 466 (m). Colorless crystals of $HC(NC_5H_3Bu^tO)_3$ suitable for X-ray were obtained from MeOH.

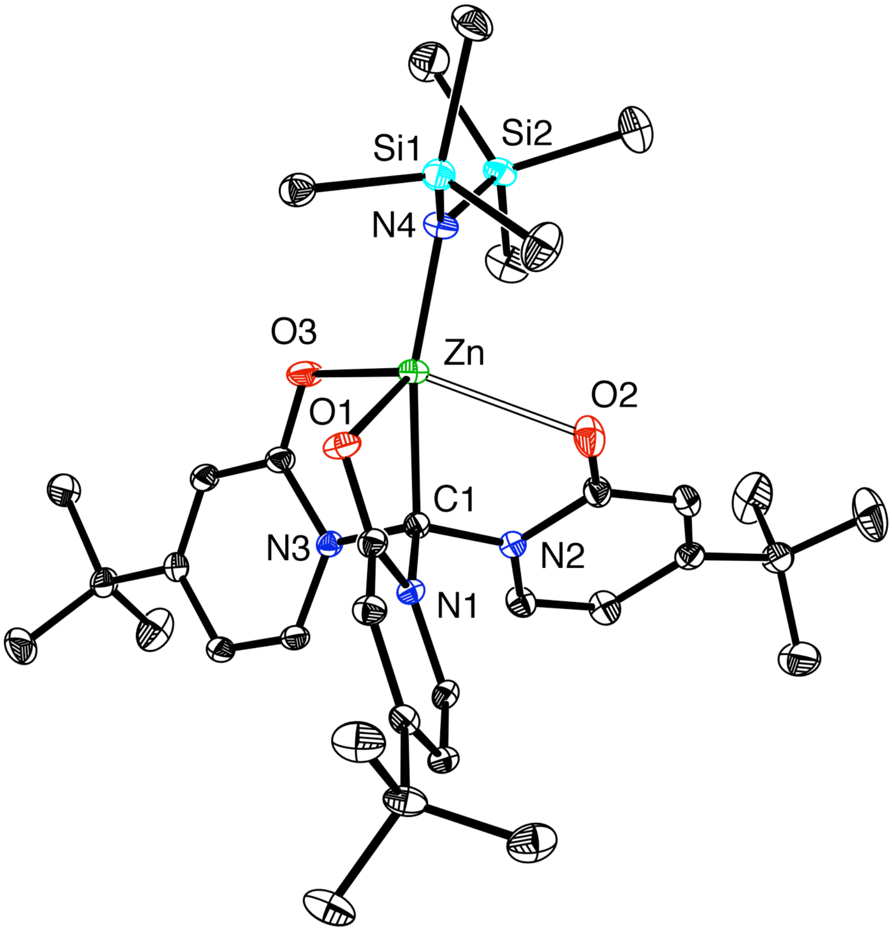


Molecular Structure of [Tpom$^{Bu^t}$]H

Synthesis of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]

A mixture of [Tpom$^{Bu^t}$]H (30.0 mg, 0.06 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (30.0 mg, 0.08 mmol) in C_6D_6 (*ca.* 1.2 mL) in an NMR tube equipped with a J. Young valve was heated at 120 °C for one week. After this period, the mixture was allowed to cool to room temperature, during which period large colorless crystals of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$] were deposited (20.0 mg, 45 %). Crystals of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$] suitable for X-ray diffraction were obtained from benzene. Analysis calcd. for [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]: C, 59.3%; H, 7.9%; N, 8.1% Found: C, 58.9%; H, 7.6%; N 7.9%. ^{1}H NMR (C_6D_6): 0.63 [s, 18H of $\{(C\underline{H}_3)_3Si\}_2NZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3$], 0.85 [s, 27H of $\{(CH_3)_3Si\}_2NZnC\{N(C_3H_3)(CC(C\underline{H}_3)_3)(CO)\}_3$], 5.79 [dd, $^3J_{H\text{-}H} = 8$, $^4J_{H\text{-}H} = 2$, 3H of $\{(CH_3)_2Si\}_2NZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3$], 6.65 [d, $^4J_{H\text{-}H} = 2$, 3H of $\{(CH_3)_2Si\}_2NZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3$], 6.93 [d, $^3J_{H\text{-}H} = 8$, 3H of $\{(CH_3)_2Si\}_2NZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 5.9 [6C of

$\{(\underline{C}H_3)_3Si\}_2NZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3]$, 29.3 [9C of $\{(CH_3)_3Si\}_2NZnC\{N(C_3H_3)(CC(\underline{C}H_3)_3)(CO)\}_3]$, 34.7 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(C_3H_3)(C\underline{C}(CH_3)_3)(CO)\}_3]$, 74.9 [1C of $\{(CH_3)_2Si\}_2NZn\underline{C}\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3]$, 107.2 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3]$, 116.0 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3]$, 132.7 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3]$, 163.3 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(C_3H_3)(\underline{C}C(CH_3)_3)(CO)\}_3]$, 164.7 [3C of $\{(CH_3)_2Si\}_2NZnC\{N(C_3H_3)(CC(CH_3)_3)(\underline{C}O)\}_3]$.

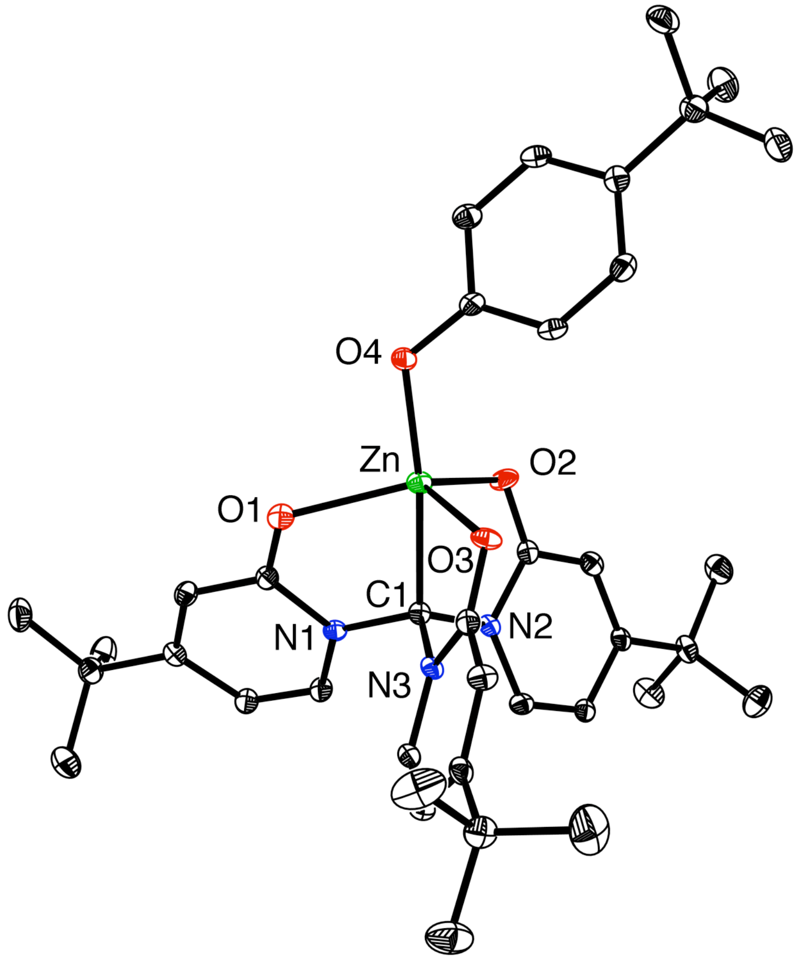


Molecular structure of [κ^4-Tpom$^{Bu^t}$]Zn[N(SiMe$_3$)$_2$]

Synthesis of $[\kappa^4\text{-Tpom}^{\mathrm{Bu^t}}]\mathrm{ZnOC_6H_4Bu^t}$

A mixture of $[\kappa^4\text{-Tpom}^{\mathrm{Bu^t}}]\mathrm{Zn[N(SiMe_3)_2]}$ (30.0 mg, 0.04) and 4-t-butylphenol (6.5 mg, 0.04 mmol) was treated with benzene (*ca.* 6 mL) and stirred for 10 minutes at room temperature. After this period, the mixture was centrifuged and the supernatant was decanted. Toluene (*ca.* 5 mL) was added and the mixture was stirred for few minutes. Then mixture was centrifuged and the supernatant was decanted. The washing procedure was repeated with pentane (*ca.* 5 mL) and the residue dried *in vacuo* to yield $[\kappa^4\text{-Tpom}^{\mathrm{Bu^t}}]\mathrm{ZnOC_6H_4Bu^t}$ as white powder (15 mg, 51%). Crystals of $[\kappa^4\text{-Tpom}^{\mathrm{Bu^t}}]\mathrm{ZnOC_6H_4Bu^t}$ suitable for X-ray diffraction were obtained from $\mathrm{CH_2Cl_2}$. Analysis calcd. for $[\kappa^4\text{-Tpom}^{\mathrm{Bu^t}}]\mathrm{ZnOC_6H_4Bu^t{\bullet}0.7CH_2Cl_2}$: C, 63.1%; H, 6.9%; N, 5.7% Found: C, 62.9%; H, 7.0%; N 5.3%. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): 1.25 [s, 27H of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(CC(C\underline{H}_3)_3)(CO)\}_3}$], 1.27 [s, 9H of $\mathrm{(C\underline{H}_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 6.56 [d, $^3J_{\mathrm{H\text{-}H}} = 7$, 3H of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$], 6.67 [d, $^3J_{\mathrm{H\text{-}H}} = 6$, 2H of $\mathrm{(CH_3)_3CC(C_2\underline{H}_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 6.79 [br, 3H of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$], 7.07 [d, $^3J_{\mathrm{H\text{-}H}} = 6$, 2H of $\mathrm{(CH_3)_3CC(C_2\underline{H}_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 7.48 [d, $^3J_{\mathrm{H\text{-}H}} = 7$, 3H of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$]. ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): 29.7 [9C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(CC(\underline{C}H_3)_3)(CO)\}_3}$], 32.0 [3C of $\mathrm{(\underline{C}H_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 33.9 [1C of $\mathrm{(CH_3)_3\underline{C}C(C_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 35.5 [3C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(C\underline{C}(CH_3)_3)(CO)\}_3}$], 109.4 [3C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 115.7 [3C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 118.6 [2C of $\mathrm{(CH_3)_3CC(\underline{C}_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 126.0 [2C of $\mathrm{(CH_3)_3CC(\underline{C}_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 133.9 [3C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 165.2 [3C of $\mathrm{(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(\underline{C}C(CH_3)_3)(CO)\}_3}$], 165.9 [3C of

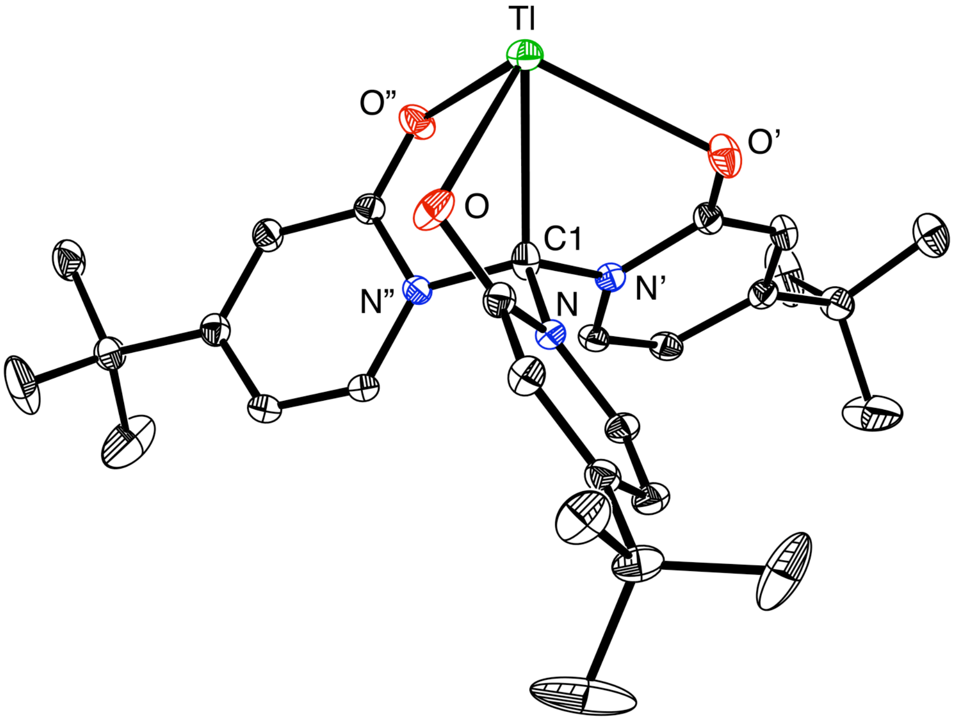
$(CH_3)_3CC(C_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(\underline{C}O)\}_3]$, not observed [1C of $(CH_3)_3C\underline{C}(C_2H_2)_2COZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3]$, not observed [1C of $(CH_3)_3CC(C_2H_2)_2\underline{C}OZnC\{N(C_3H_3)(CC(CH_3)_3)(CO)\}_3]$.



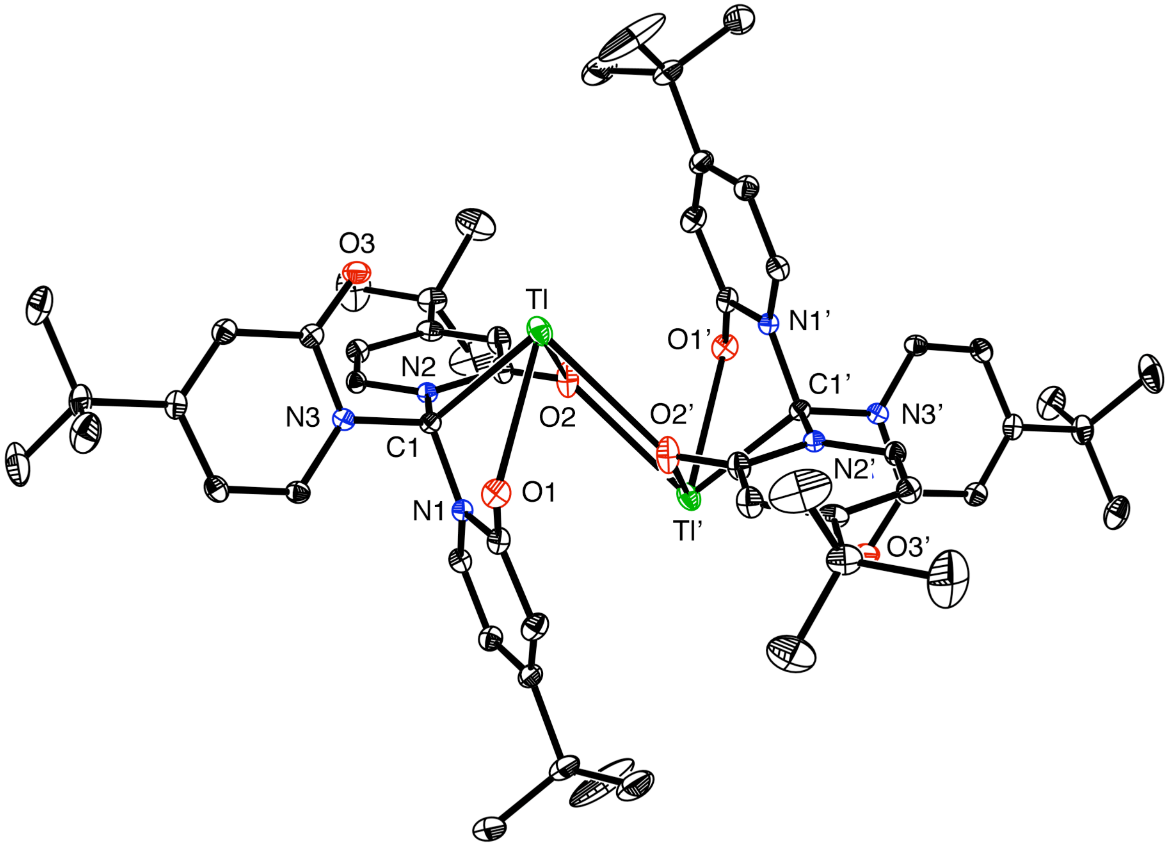
Molecular Structure of [κ^4-Tpom$^{Bu^t}$]ZnO$C_6H_4Bu^t$

Synthesis of [Tpom$^{Bu^t}$]Tl

A mixture of [Tpom$^{Bu^t}$]H (10 mg, 0.02 mmol) and $TlN(SiMe_3)_2$ (20 mg, 0.05 mmol) in an NMR tube equipped with a J. Young valve was treated with C_6D_6 (*ca.* 1.2 mL) was monitored by 1H NMR spectroscopy. The mixture was shaken occasionally and, after a period of 4 days, the solvent was lyophilized and the solid obtained was washed with pentane (*ca.* 2 mL) and dried *in vacuo* to give [Tpom$^{Bu^t}$]Tl as an amber solid (7.0 mg, 49%). Crystals of [Tpom$^{Bu^t}$]Tl suitable for X-ray diffraction were obtained by the slow diffusion of hexane into a toluene solution, whereas crystals of {[Tpom$^{\mathrm{Bu^t}}$]Tl}$_2$ suitable for X-ray diffraction were obtained by the slow diffusion of pentane into a benzene solution. ^{1}H NMR (C_6D_6): 0.95 [s, 27H of $\mathrm{TlC\{N(C_3H_3)(CC(C\underline{H}_3)_3)(CO)\}_3}$], 5.75 [dd, $^3J_{H\text{-}H}$ = 8, $^4J_{H\text{-}H}$ = 2, 3H of $\mathrm{TlC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$], 6.62 [d, $^4J_{H\text{-}H}$ = 2, 3H of $\mathrm{TlC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$], 6.78 [d, $^3J_{H\text{-}H}$ = 8, 3H of $\mathrm{TlC\{N(C_3\underline{H}_3)(CC(CH_3)_3)(CO)\}_3}$]. ^{13}C{^{1}H} NMR ($C_6D_6$): 29.6 [9C of $\mathrm{TlC\{N(C_3H_3)(CC(\underline{C}H_3)_3)(CO)\}_3}$], 34.6 [3C of $\mathrm{TlC\{N(C_3H_3)(C\underline{C}(CH_3)_3)(CO)\}_3}$], 107.1 [3C of $\mathrm{TlC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 117.3 [3C of $\mathrm{TlC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 133.9 [3C of $\mathrm{TlC\{N(\underline{C}_3H_3)(CC(CH_3)_3)(CO)\}_3}$], 161.4 [3C of $\mathrm{TlC\{N(C_3H_3)(\underline{C}C(CH_3)_3)(CO)\}_3}$], 164.2 [3C of $\mathrm{TlC\{N(C_3H_3)(CC(CH_3)_3)(\underline{C}O)\}_3}$]. The self-diffusion constant for [Tpom$^{\mathrm{Bu^t}}$]Tl was determined by pulsed gradient spin-echo (PGSE) diffusion NMR spectroscopic experiments employing the Bruker stebpg1s pulse sequence, and the value of 6.27×10^{-10} m^{2}s^{-1} is comparable to that of [Tpom$^{\mathrm{Bu^t}}$]H, 6.43×10^{-10} m^{2}s^{-1}, indicating that both molecules have similar hydrodynamic radii and that [Tpom$^{\mathrm{Bu^t}}$]Tl is a monomer in toluene solution.

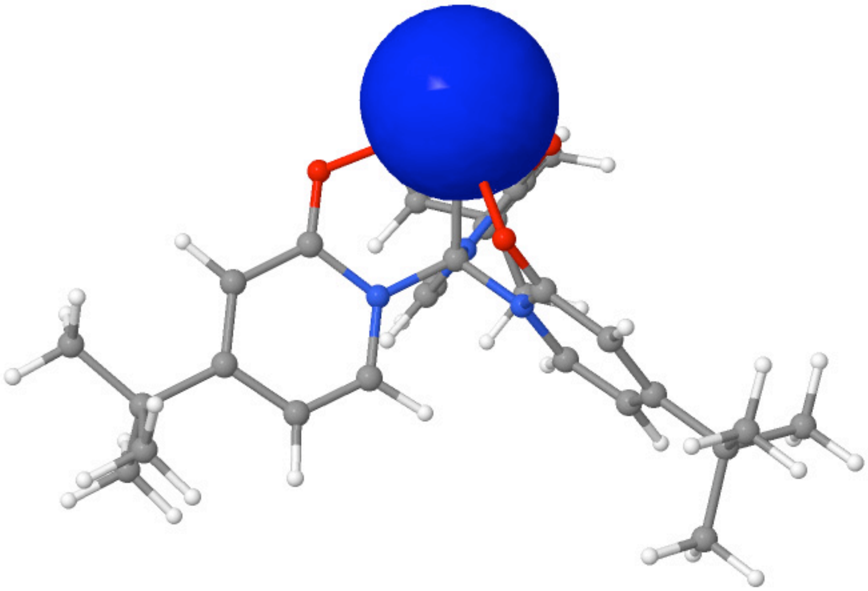


Molecular Structure of [κ^4-Tpom$^{\mathrm{Bu^t}}$]Tl obtained by diffusion of hexane into a toluene solution.



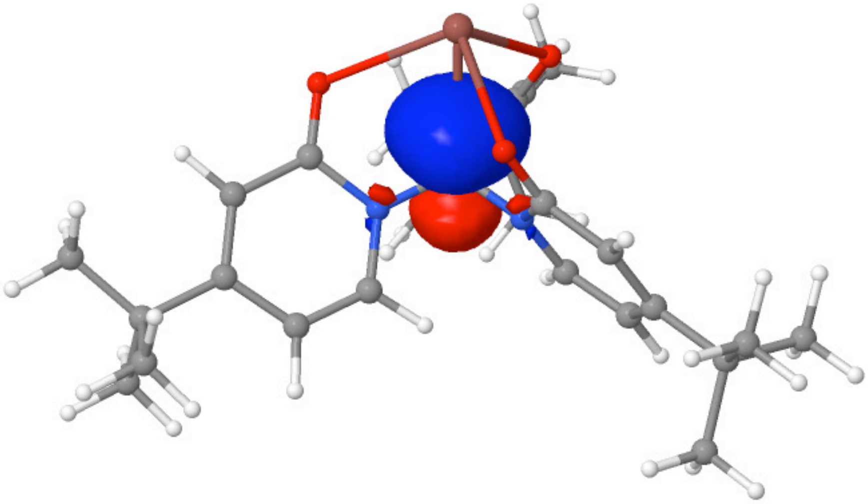
Molecular Structure of {[κ^3-Tpom$^{Bu^t}$]Tl}$_2$ obtained by diffusion of pentane into a benzene solution

Cartesian coordinates for geometry optimized [Tpom$^{Bu^t}$]Tl are listed in Table 2 and Fenske-Hall molecular orbitals and natural bond orbitals are illustrated below.



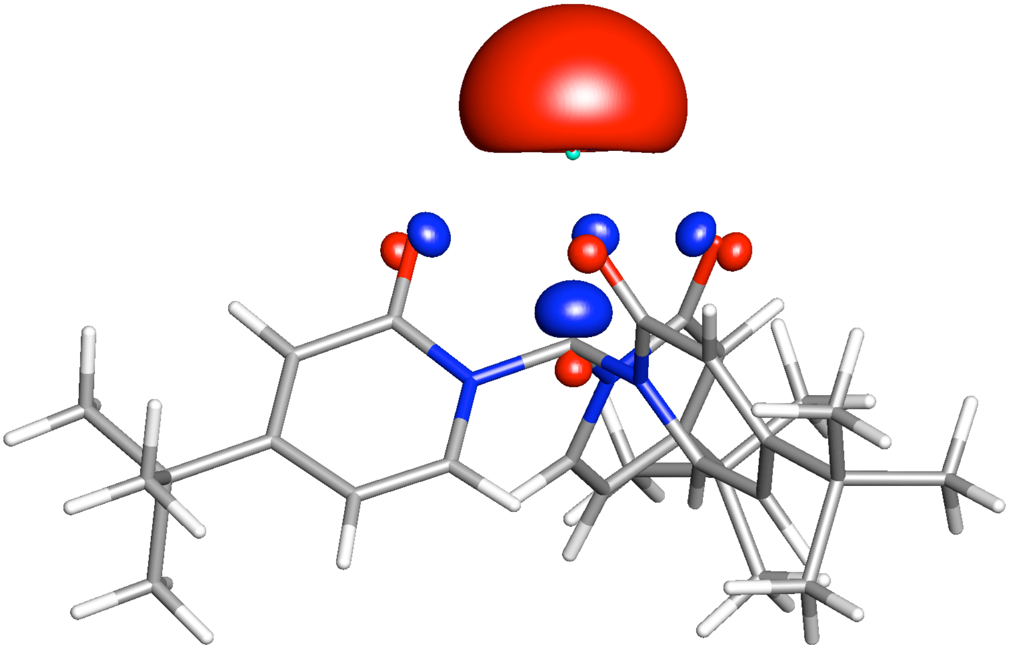
Natural bond orbital for Tl lone pair

(96.76% 6s and 3.24% 6p character)

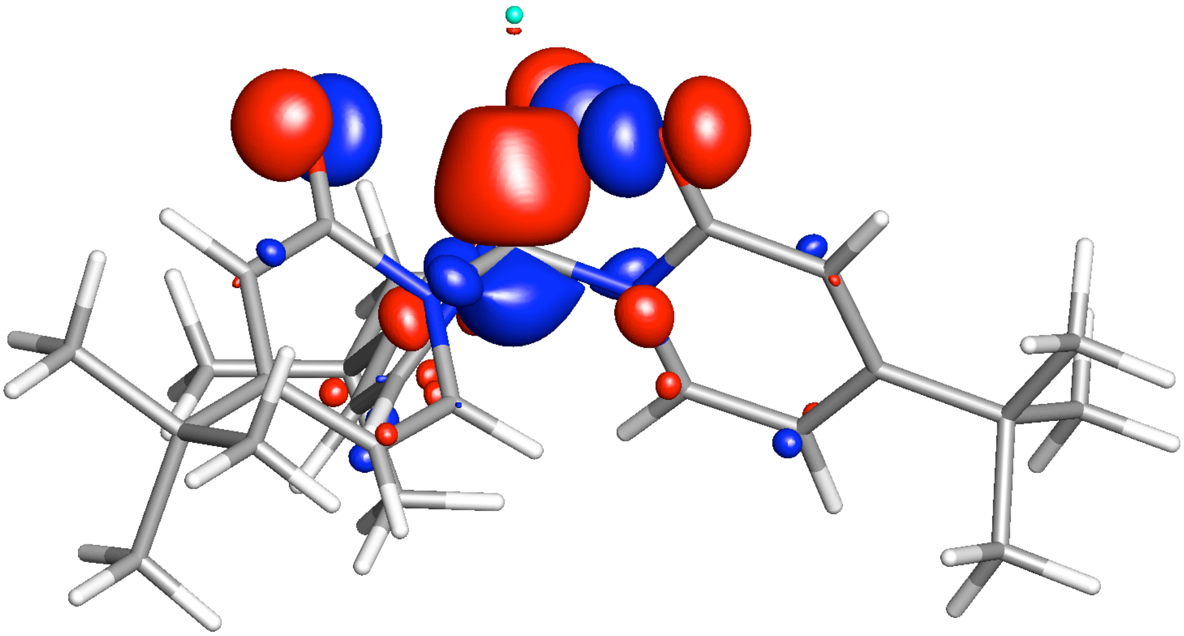


Natural bond orbital for C lone pair

(22.68% 2s, 77.30% 2p and 0.02% of 3d character)



HOMO (Tl lone pair)



HOMO–1 (C lone pair)

Table 1. Crystal, intensity collection and refinement data.

	[Tpom]H	**[Tpom$^{Bu^t}$]H**
lattice	Trigonal	Monoclinic
formula	$C_{16}H_{13}N_3O_3$	$C_{28}H_{37}N_3O_3$
formula weight	295.29	463.61
space group	*R*3	$P2_1/c$
a/Å	15.486(3)	11.8366(15)
b/Å	15.486(3)	18.801(2)
c/Å	5.0769(11)	12.2176(16)
α/°	90	90
β/°	90	106.441(2)
γ/°	120	90
V/Å^3	1054.4(4)	2607.7(6)
Z	3	4
temperature (K)	125(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.395	1.181
μ (Mo Kα), mm^{-1}	0.099	0.077
θ max, deg.	31.64	30.75
no. of data collected	5315	41441
no. of data used	1540	8080
no. of parameters	67	316
R_1 [$I > 2\sigma(I)$]	0.0404	0.0569
wR_2 [$I > 2\sigma(I)$]	0.1037	0.1401
R_1 [all data]	0.0451	0.0983
wR_2 [all data]	0.1063	0.1628
GOF	1.060	1.023
R_{int}	0.0380	0.0660

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

	[κ^3-Tpom]Zn[N(SiMe$_3$)$_2$]	**[κ^4-Tpom$^{Bu^t}$]-Zn[N(SiMe$_3$)$_2$]**
lattice	Triclinic	Orthorhombic
formula	$C_{26}H_{40}N_4O_4Si_2Zn$	$C_{46}H_{66}N_4O_3Si_2Zn$
formula weight	594.17	844.58
space group	*P-1*	$P2_12_12_1$
a/Å	10.347(3)	13.8655(11)
b/Å	10.513(3)	15.0021(12)
c/Å	15.117(17)	22.8550(18)
α/°	102.776(5)	90
β/°	105.658(5)	90
γ/°	97.886(5)	90
V/Å^3	1509.9(8)	4754.1(7)
Z	2	4
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.307	1.180
μ (Mo Kα), mm^{-1}	0.929	0.608
θ max, deg.	30.63	30.55
no. of data collected	24546	76604
no. of data used	9236	14503
no. of parameters	342	520
R_1 [$I > 2\sigma(I)$]	0.0508	0.0361
wR_2 [$I > 2\sigma(I)$]	0.0768	0.0797
R_1 [all data]	0.1087	0.0536
wR_2 [all data]	0.0905	0.0877
GOF	1.002	1.019
R_{int}	0.0708	0.0473

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

	[κ^4-Tpom$^{Bu^t}$]ZnOC$_6$H$_4$Bu^t	**[Tpom$^{Bu^t}$]Tl**
lattice	Monoclinic	Trigonal
formula	$C_{42}H_{57}Cl_8N_3O_4Zn$	$C_{28}H_{36}N_3O_3Tl$
formula weight	1016.88	666.97
space group	$P2_1/n$	R-3
a/ Å	14.5805(16)	15.492(4)
b/ Å	14.0968(15)	15.492(4)
c/ Å	24.168(3)	19.782(5)
α/ °	90	90
β/ °	93.703(2)	90
γ/ °	90	120
V/ Å^3	4957.2(9)	4111.6(16)
Z	4	6
temperature (K)	150(2)	130(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.363	1.616
μ (Mo Kα), mm^{-1}	0.968	5.925
θ max, deg.	24.71	30.70
no. of data collected	43118	21563
no. of data used	8462	2818
no. of parameters	535	109
R_1 [$I > 2\sigma(I)$]	0.0690	0.0383
wR_2 [$I > 2\sigma(I)$]	0.1524	0.0873
R_1 [all data]	0.1269	0.0508
wR_2 [all data]	0.1723	0.0927
GOF	1.133	1.030
R_{int}	0.1209	0.0739

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

	$\{[\mathrm{Tpom}^{\mathrm{Bu^t}}]\mathrm{Tl}\}_2$
lattice	Monoclinic
formula	$C_{56}H_{72}N_6O_6Tl_2$
formula weight	1333.94
space group	$P2_1/n$
a/ Å	11.9498(15)
b/ Å	10.7516(13)
c/ Å	21.365(3)
α/ °	90
β/ °	92.803(2)
γ/ °	90
V/ Å^3	2741.7(6)
Z	2
temperature (K)	150(2)
radiation (λ, Å)	0.71073
ρ (calcd.), g cm^{-3}	1.616
μ (Mo Kα), mm^{-1}	5.924
θ max, deg.	32.03
no. of data collected	46294
no. of data used	9456
no. of parameters	325
R_1 [$I > 2\sigma(I)$]	0.0319
wR_2 [$I > 2\sigma(I)$]	0.0720
R_1 [all data]	0.0522
wR_2 [all data]	0.0784
GOF	1.030
R_{int}	0.0442

Table 2. Cartesian Coordinates for Geometry Optimized Structure of [Tpom$^{\mathrm{Bu^t}}$]Tl.

[Tpom$^{\mathrm{Bu^t}}$]Tl

-1480.69342327206 Hartrees

atom	x	y	z
Tl	-0.007073257	-0.005740297	5.696597513
O	1.934943045	1.277553268	4.495005443
N	0.524351765	1.278928468	2.669915594
C	-0.00425187	-0.006458295	3.129438362
C	1.538710846	1.858075805	3.467592075
C	2.061217616	3.117003615	3.002776322
H	2.844601074	3.527205422	3.626426019
C	1.600599825	3.763453864	1.881518183
C	2.159551246	5.107065595	1.389863846
C	2.714059091	4.926327838	-0.044756573
H	1.942341435	4.591971607	-0.744897729
H	3.525127639	4.19058726	-0.062755344
H	3.111138772	5.877097766	-0.417599495
C	1.021478962	6.156473013	1.372989306
H	0.608376755	6.303490595	2.376206927
H	0.200199517	5.86226972	0.712517564
H	1.404239112	7.120070512	1.018358512
C	3.29381858	5.631682083	2.288558761
H	2.951856816	5.804964372	3.313881573
H	3.663162964	6.585141224	1.896683764
H	4.139483402	4.937106735	2.322482743
C	0.543957854	3.13758469	1.151502454

H	0.113653003	3.599192799	0.270928134
C	0.054626046	1.932135655	1.559382558
H	-0.747231903	1.437461858	1.026064248
O	-2.077824626	1.06859008	4.472081143
N	-1.380502852	-0.186883669	2.666728642
C	-2.386740099	0.422542241	3.45389206
C	-3.738362187	0.249550069	2.988332828
H	-4.482886023	0.738135911	3.603072726
C	-4.071575235	-0.486887245	1.877258657
C	-5.51543148	-0.668587464	1.384938468
C	-5.627945527	-0.112144103	-0.055939262
H	-4.954299872	-0.625988818	-0.748576601
H	-5.387716518	0.956020468	-0.084456314
H	-6.649760239	-0.23949879	-0.430624269
C	-5.867102903	-2.176276852	1.38244938
H	-5.793993766	-2.598349569	2.39003085
H	-5.204547062	-2.752303011	0.72937179
H	-6.893197422	-2.322050192	1.026474686
C	-6.534002613	0.06859144	2.273663217
H	-6.518505238	-0.303569125	3.302986457
H	-7.54440146	-0.085229014	1.880757664
H	-6.347917562	1.147250961	2.296781843
C	-3.004689231	-1.108236296	1.15872644
H	-3.191895579	-1.723099416	0.28661202
C	-1.715060779	-0.933402335	1.566243465
H	-0.888774824	-1.394472435	1.040329207
O	0.154934838	-2.332592717	4.489036582
N	0.844555822	-1.103563485	2.662812326

C	0.852949748	-2.27214517	3.460533136
C	1.694176265	-3.344742075	2.995027539
H	1.671138609	-4.227058051	3.621065663
C	2.480547332	-3.261451282	1.871807635
C	3.38144461	-4.405135069	1.382002002
C	2.948616565	-4.809257793	-0.04890603
H	3.026634357	-3.975346453	-0.75324801
H	1.912122719	-5.162800209	-0.060638945
H	3.586675615	-5.618672624	-0.42089456
C	4.851211726	-3.919105366	1.356739594
H	5.183654006	-3.622994487	2.357004415
H	4.989991909	-3.062307777	0.690481352
H	5.507040359	-4.723379743	1.004786947
C	3.294002356	-5.647082182	2.287131302
H	3.615675307	-5.42719134	3.310105507
H	3.947357353	-6.434081289	1.89617418
H	2.27680582	-6.050115678	2.327299806
C	2.447651784	-2.035782425	1.138284025
H	3.056269669	-1.888400813	0.254248152
C	1.638542698	-1.017775209	1.547542893
H	1.598409236	-0.078133321	1.011389272

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