Supporting information for:

"Synthesis of Lithium Corrole and its Use as a Reagent for the Preparation of Cyclopentadienyl Zirconium and Titanium Corrole Complexes"

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A. General Considerations

Unless otherwise noted, all reactions were performed using standard Schlenk and N_2-atmosphere glovebox techniques. Glassware and cannulae were stored in an oven at *ca.* 180 ºC. Solvents were dried by passing through a column of activated alumina and degassed with nitrogen.[1] C_6D_6 was dried over Na/benzophenone, and vacuum transferred. All NMR spectra were obtained in C_6D_6 at ambient temperature using Bruker AVB-400 or AVQ-400 spectrometers. ^1H NMR chemical shifts (δ) were calibrated relative to residual solvent peak. UV-visible spectra were determined with a Varian Cary 50UV-vis spectrophotometer using a 1 mm quartz cell. Mass spectral data (ESI-MS, positive mode) were obtained at the University of California, Berkeley Microanalytical Facility, using vacuum-dried samples dissolved in dry THF. X-ray crystal diffraction analyses were performed at the University of California, Berkeley CHEXRAY facility. Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. $LiN(SiMe_3)_2$[2] and 5-(2,4,6-trimethylphenyl)dipyrromethane[3] were prepared according to literature procedures. 4-methoxybenzaldehyde, hydrazine (1.0 M in THF), *p*-chloranil were obtained from Aldrich. Cyclopentadienyl zirconium(IV) trichloride and pentamethylcyclopentadienyl titanium(IV) trichloride were obtained from Strem Chemicals.

B. Synthesis and characterization of free base corrole and of complexes 1, 2, and 3

5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole (Mes_2(*p*-OMePh)corroleH_3) was prepared according to a modified literature procedure[4] under benchtop conditions with solvents used as received. As much as possible, flasks were covered with aluminum foil to reduce exposure to light. 5-(2,4,6-trimethylphenyl)dipyrromethane (2.64 g, 10 mmol) and 4-methoxybenzaldehyde (612 µL, 5.0 mmol) were dissolved in methanol (1 L). Concentrated hydrochloric acid (36 %, 50 mL) was combined with 500 mL distilled water, and the acid solution was added to the methanol solution with stirring, immediately producing a peach-colored suspension. The mixture was stirred for two hours at room temperature, and then extracted with chloroform (5 x 200 mL, or until the aqueous layer is pale yellow). The organic extracts were combined, dried over sodium sulfate, filtered, and diluted to 1.25 L. *p*-Chloranil (3.69 g, 15 mmol) was added and the reaction was stirred overnight at room temperature. The solution was concentrated to 100 mL by rotary evaporation, then filtered through a silica pad and eluted with methylene chloride. The combined eluents were concentrated to dryness, and dissolved in 25 mL THF. To this solution was added hydrazine solution (1.0 M in THF, 10 mL) and the solution was stirred for 10 minutes. The solution was then concentrated to dryness. Column chromatography on silica (ramped 100% hexane to 1:1 methylene chloride: hexane, $R_f = 0.55$ in 1:1 methylene chloride:hexane) provides pure corrole (450 mg, 14% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (d, $J = 4.1$ Hz, 2H, β-*H*), 8.49 (d, $J = 4.6$ Hz, 2H, β-*H*), 8.47 (d, $J = 4.6$ Hz, 2H, β-*H*), 8.31 (s, 2H, β-*H*), 8.06, 7.25 (AA'BB', $J = 8.6$ Hz), 7.26 (s(broad), 4H, $C_6H_2(CH_3)_3$), 4.06 (s, 3H, OCH_3), 2.59 (s, 6H, $C_6H_2(CH_3)_2(p\text{-}CH_3)$), 1.92 (s, 12H, $C_6H_2CH_3(o\text{-}CH3)_2$), (-3) – (-1) (s(broad), 3H, N*H*). UV-Vis (CH_2Cl_2, nm) 407, 427, 566, 605, 636. ESI-MS (+) Calcd: 641.3275 for $C_{44}H_{41}N_4O$, observed 641.3304. M.p. > 300 °C.

Note: The major monomeric byproduct of this reaction is $Mes_2(p\text{-}OMePh)_2$porphyrin (R_f = 0.5 in 1:1 methylene chloride: hexane, vs. R_f = 0.55 in 1:1 methylene chloride: hexane for the corrole). The porphyrin can generally be removed by careful monitoring of the silica plug eluent before reduction of the product with hydrazine. If these two products fail to separate by column chromatography, the corrole can be suspended in a minimum volume of hot hexane, cooled, and filtered to remove the porphyrin with minimal loss of yield.

Trilithium 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole hexakis(tetrahydrofuran) (Mes_2(*p*-OMePh)corroleLi_3·6THF) (**1·6THF**). Mes_2(*p*-OMePh)corroleH_3 (300 mg, 0.47 mmol) and lithium bis-trimethylsilylamide (236 mg, 1.41 mmol) were combined in a Schlenk flask. The flask was cooled to -40 ºC and 15 mL THF was added by cannula. The solution was allowed to warm to room temperature and stirred for two hours. The volume of the solution was reduced to ~7 mL under vacuum, 2-3 mL of hexane was added by cannula, and the solution was cooled to -40 ºC and cannula filtered to generate a deep green solid (380 mg, 74% yield). Crystals suitable for X-ray diffraction were grown by vapor diffusion of hexane into a concentrated solution of dimethoxyethane at room temperature. ^{1}H NMR (C_6D_6): 8.91 (m, 2H, β-*H*), 8.85 (m, 2H, β-*H*), 8.70 (s(broad), 2H, β-*H*), 8.51 (s(broad), 2H, β-*H*), 8.35 (d, *J* = 7.9 Hz, 2H, C_6H_3H-OMe), 7.38 (s, 4H, $C_6H_2Me_3$), 7.25 (d, *J* = 7.9 Hz, 2H, C_6H_3H-OMe), 3.57 (s, 3H, OCH_3), 2.59 (s, 6H, $C_6H_2Me_2(p\text{-}CH_3)$), 2.40 (m, 24H, THF), 2.31 (s, 12H, $C_6H_2Me(o\text{-}CH_3)_2$), 0.79 (qt, *J* = 11.4, 7.2 Hz, 24H, THF). ^{7}Li NMR (C_6D_6, referenced to LiCl in H_2O): -8.40. UV-vis (nm): 422, 446, 587, 626. ESI-MS (+) Calcd:

644.3122 for $C_{44}H_{37}N_4O_1Li_1$, 651.3282 for $C_{44}H_{37}N_4O_1Li_2$ Observed: 644.3189, 651.3557. Mp: decomposition above 350 ºC.

Cyclopentadienyl zirconium(IV) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl) corrole (CpZrMes$_2$(*p*-OMePh)corrole) (**2**). Mes$_2$(*p*-OMePh)corroleLi$_3$·6THF (100 mg, 0.092 mmol), and cyclopentadienyl zirconium(IV) trichloride (36 mg, 0.10 mmol) were combined in a Schlenk flask. The flask was cooled to -40 ºC and 10 mL THF was added by cannula. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and the resulting solid was taken up in hexane. The solution was cooled to -40 ºC and cannula filtered to generate deep red microcrystals (59 mg, 81% yield). Crystals suitable for X-ray diffraction were grown by slow evaporation of pentane at -40 ºC. ^{1}H NMR (400 MHz, C_6D_6): δ 8.88 (d, *J* = 4.0 Hz, 2H, β-*H*), 8.84 (d, *J* = 4.3 Hz, 2H, β-*H*), 8.78 (d, *J* = 4.4 Hz, 2H, β-*H*), 8.70 (d, *J* = 4.0 Hz, 2H, β-*H*), 8.33 (dd, *J* = 8.4, 2.3 Hz, 1H, C_6H_3H-OMe), 7.62 (dd, *J* = 8.4, 2.3 Hz, 1H, C_6H_3H-OMe), 7.39-7.36 (m, 4H, $C_6H_2Me_3$), 7.29 (dd, *J* = 8.3, 2.7 Hz, 1H, C_6H_3H-OMe), 7.00 (dd, *J* = 8.4, 2.8 Hz, 1H, C_6H_3H-OMe), 3.52 (s, 3H, OCH_3), 3.11 (s, 5H, C_5H_5), 2.60 (s, 6H, $C_6H_2Me_2CH_3$), 2.53 (s, 6H, $C_6H_2Me_2CH_3$), 1.44 (s, 6H, $C_6H_2Me_2CH_3$).^{13}C NMR (101 MHz, C_6D_6): δ 159.84, 144.11, 142.14, 141.65, 139.97, 139.30 (d, *J* = 4.0 Hz), 137.59 (d, *J* = 15.9 Hz), 135.39, 134.76, 128.77, 128.48 (d, *J* = 12.2 Hz), 126.77 (d, *J* = 12.6 Hz), 124.92, 119.51, 117.16, 113.33, 113.03, 110.30, 101.24, 67.27, 55.03, 22.35, 21.60, 20.52. UV-vis (nm): 421, 583. ESI-MS (+) Calcd: 792.2400 for $C_{49}H_{42}O_1N_4Zr_1$ Observed: 792.2426. Mp: decomposition above 350 ºC.

Pentamethylcyclopentadienyl titanium(IV) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)-corrole. (Cp*TiMes$_2$(*p*-OMePh)corrole) (**3**). Mes$_2$(*p*-OMePh)corroleLi$_3$·6THF (60 mg, 0.055 mmol), and pentamethylcyclopentadienyl titanium(IV) trichloride (36 mg, 0.061 mmol) were combined in a vial in the glovebox and 6 mL THF was added. The solution was stirred overnight. The solvent was removed under vacuum and the resulting solid was taken up in hexane. The solution was cooled to -40 ºC and filtered to generate deep red microcrystals (29 mg, 78 % yield). Crystals suitable for X-ray diffraction were grown by vapor diffusion of hexane into a concentrated solution of toluene at room temperature. ^{1}H NMR (C_6D_6): δ 8.80 (d, *J* = 4.2 Hz, 2H, β-*H*), 8.76 (d, *J* = 4.5 Hz, 2H, β-*H*), 8.62, (d, *J* = 4.6 Hz, 2H, β-*H*), 8.55 (d, *J* = 4.2 Hz, 2H, β-*H*), 7.56 (d, *J* =8.4 Hz, 1H, C_6H_3H-OMe), 7.42 (s, 2H, $C_6H_2Me_3$), 7.33 (dd, *J* = 10.6, 4.1 Hz, 1H, C_6H_3H-OMe), 7.13 (d, J = 6.2 Hz, 1H, C_6H_3H-OMe), 6.94 (dd, 10.6, 4.1 Hz, 1H, C_6H_3H-OMe), 6.88 (s, 2H, $C_6H_2Me_3$), 3.54 (s, 3H, OCH_3) 3.26 (s, 6H, $C_6H_2Me_2CH_3$), 2.44 (s, 6H, $C_6H_2Me_2CH_3$), 0.45 (s, 6H, $C_6H_2Me_2CH_3$), -0.05 (s, 15H, $C_5(CH_3)_5$).UV-vis (nm): 425, 573. ESI-MS (+) Calcd: 820.3615 for $C_{54}H_{52}O_1N_4Ti_1$ Observed: 820.3641. Mp: decomposition above 350 ºC.

C. Titration of free base corrole with LiN(SiMe$_3$)$_2$

In the glovebox, a 2.0 mM solution of free base corrole (Solution A) was prepared by dissolving 12.8 mg corrole in 10 mL THF. A 30 mM solution of LiN(SiMe$_3$)$_2$ (Solution B) was prepared by dissolving 10.0 mg LiN(SiMe$_3$)$_2$ in 2 mL THF. 0.05 mL A, 0.95 mL THF were measured into a 1 mm quartz Schlenk cuvette and the UV-visible spectrum of the free-base corrole was recorded at 0.1 mM concentration. 3 mL A (0.006

mmol) and 3 mL THF were measured into a vial, and 0.2 mL (0.006 mmol, 1 equiv) B was added. 0.155 mL (0.00015 mmol) of the solution was removed and diluted to 1.5 mL with THF to produce a 0.1 mM solution; the UV-visible spectrum of this solution was recorded. This procedure was repeated in such a manner as to ensure that 1.0 equiv. of $LiN(SiMe_3)_2$ was added to the actual amount of corrole remaining in the reaction vial, and that all UV-visible spectra were obtained at 0.1 mM concentration.

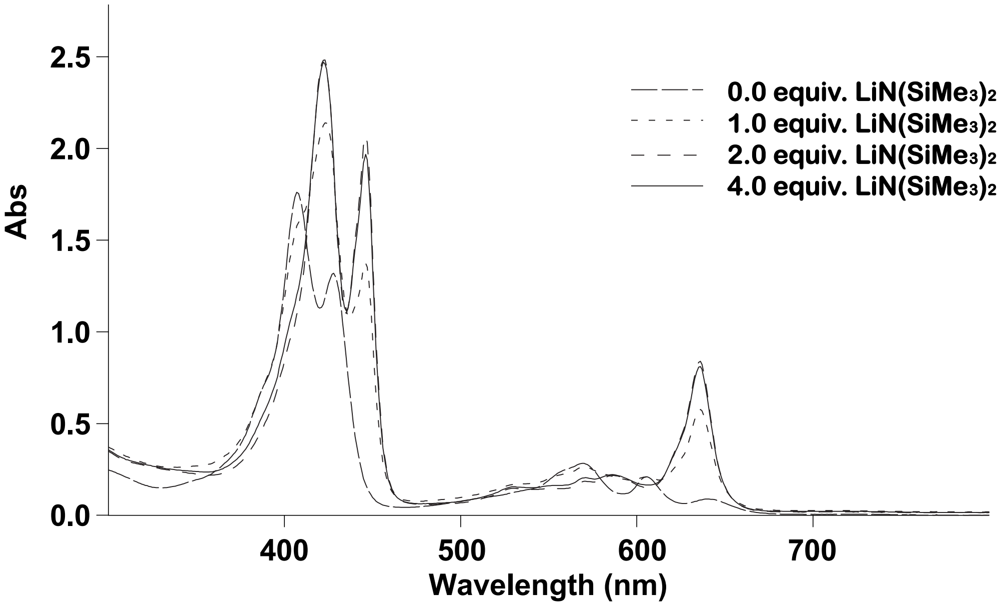

Figure S1. Titration of free-base corrole with $LiN(SiMe_3)_2$ as monitored by UV-visible spectroscopy.

D. Determination of molecular structure by single-crystal X-ray diffraction

X-ray structural determinations were performed on a Bruker MicroSTAR-H APEX II or Bruker APEX II Quazar diffractometer. Both are Kappa Geometry with DX. Both are 3-circle diffractometers that couple a CCD detector[5] with a sealed-tube source of monochromated Cu-Kα (MicroSTAR) or Mo Kα radiation (Quazar). A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan® loop. The loop was transfered to the diffractometer, centered in the beam, and cooled by a nitrogen flow low- temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\ \sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[6] All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).[7] Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. ORTEP diagrams were created using the ORTEP-3 software package and POV-ray.[8]

Table S1 shows crystallographic data for corrole complexes **1**, **2**, and **3**.

Table S1. Crystallographic data for **1·4DME**, **2**, and **3**.

Compound	1	2	3
Formula	$C_{60}H_{77}Li_3N_4O_9$	$C_{49}H_{42}N_4OZr$	$C_{54}H_{52}N_4OTi$
Form. wt. (amu)	1019.08	794.09	820.90
Wavelength (Å)	1.54178	0.71073	1.54178
Space Group	$P2_1/n$	Pbca	P-1
a (Å)	14.9866(8)	19.2272(9)	10.8502(10)
b (Å)	23.6356(12)	19.8419(10)	14.0504(13)
c (Å)	16.4784(9)	20.2471(9)	14.6264(13)
α (º)	90	90	96.477(4)
β (º)	101.871(4)	90	93.780(4)
γ (º)	90	90	104.095(4)
V (Å^3)	5712.1(5)	7724.4(6)	2138.7(3)
Z	4	8	2
ρ_{calcd} (g/cm^3)	1.185	1.366	1.275
F_{000}	2184	3296	868
μ (mm^{-1})	0.623	0.328	2.037
T_{min}/T_{max}	3.32/67.77	1.79/26.18	3.06/68.13
Refl'ns collected	55039	127751	34085
Indep. refl'ns	10121	7116	7564
R_{int}	0.0391	0.0784	0.0255
R_1, wR_2	0.0693/0.1905	0.0354/0.0781	0.0418/0.1153
R_1, (all data)	0.0879	0.0598	0.0435
GoF	1.036	1.044	1.043
Res. peak/hole (e$^-$/ Å^3)	0.688/-0.363	0.345/-0.560	0.282/-0.333

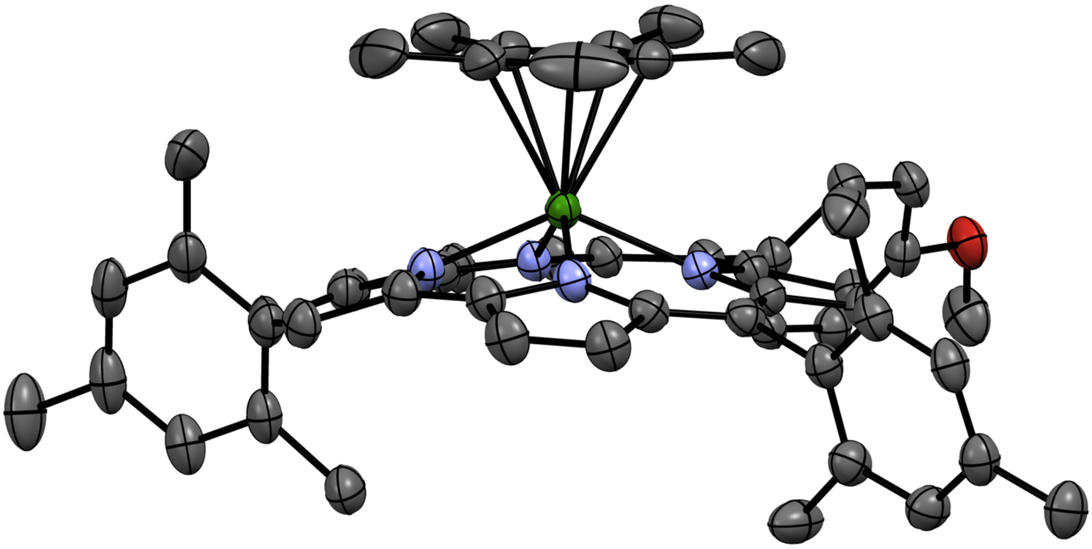

Figure S2. Molecular structure of pentamethylcyclopentadienyl titanium(IV) corrole **3** determined by single-crystal X-ray diffraction. The average Ti-N bond distance is 2.049(3) Å and the Ti sits 0.820 Å from the N_4 plane. H atoms have been omitted for clarity; thermal ellipsoids at 50 % probability level.

E. References

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