Supporting Information

Five-coordinate M^{II}-semiquinonate (M = Fe, Mn, Co) complexes: Reactivity

models of the catechol dioxygenases

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Experimental Details

General Materials and Methods

All manipulations were carried out either in an inert atmosphere glovebox or on a Schlenk line. Unless otherwise noted, all reagents were purchased from commercial sources and were used without further purification. MnI₂ (anhydrous flakes) purchased from Sigma-Aldrich was a gift from Louise Liable-Sands at Widener University. Anhydrous FeI₂ and CoI₂ were purchased from Strem. THF, Diethyl ether, pentane, and acetonitrile were dried by passing through activated alumina, sparged with N₂, and cannula transferred into the solvent bottles. THF, and acetonitrile was further dried over 4 Å or 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves. [PhTt^{tBu}]Tl,¹ TI(phenSQ),² Tl(3,5-DBSQ),² [PhTt^{tBu}]Fe(PMe₃)³ and [PhTt^{Bu}]Co(PMe₃)⁴ were prepared following the published procedures. NMR spectra were recorded on a Bruker AVIII 400 spectrometer. Chemical shifts (δ) were referenced to residual protons in the deuterated solvent. FT-IR spectra were recorded Magna-IR ESP 560 spectrometer. Electronic spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer using screw-top quartz cuvettes with a 1 cm path-length. Low temperature UV-vis experiments were conducted using a Unisoku Scientific Instruments cryostat coupled to a Varian Cary 50 UV-vis spectrophotometer. Solution state magnetic moments were determined using the Evans method.⁵ Liquid injection field desorption ionization (LIFDI) mass spectroscopy,⁶ high resolution electron ionization (EI) mass spectroscopy and chemical ionization (CI) mass spectroscopy were performed on a Waters GCT Premier mass spectrometer.

Synthesis

[PhTt^{tBu}]FeI

Anhydrous FeI₂ (310 mg, 1.0 mmol) was dissolved in 50 mL of CH₃CN. [PhTt^{tBu}]Tl (602 mg, 1.0 mmol) was added in small portions to the stirring solution of FeI₂. TII precipitated immediately as a yellow solid and the color of the solution changed to pale yellowish brown. After stirring for 2 hr, the reaction mixture was filtered through Celite removing TII and the solvent was removed in vacuo. The residue was extracted with pentane/diethyl ether (v:v = 5:1) and was filtered through Celite. Removing the solvent under reduced pressure afforded a pale green solid. Recrystallization by slow evaporation of the pentane solution afforded yellow crystals (87 mg, 15%). ¹H NMR (C₆D₆): δ 14.6 (27H, br, C(CH₃)₃S), 14.2 (2H, s, *m*-(C₆H₅)B), 9.1 (1H, s, *p*-(C₆H₅)B), 8.2 (2H, s, *o*-(C₆H₅)B). UV-vis (THF): λ_{max} (ε , M⁻¹ cm⁻¹) 264 (3620), 315 (3140), 368 (sh). FTIR (KBr): 3058, 3040, 2961, 2894, 2861, 1456, 1426, 1399, 1366, 1260, 1160, 1027, 951, 893, 869, 748, 700, 576, 506. LIFDI-MS: calcd. for C₂₁H₃₈BFeIS₃ (M)⁺ 580.0627 *m/z*, found (M)⁺ 580.0632 *m/z* (100%). μ_{eff} (C₆D₆) = 5.35(3) μ_{B} .

[PhTt^{tBu}]MnI

Anhydrous MnI_2 (309 mg, 1.0 mmol) was dissolved in 50 mL of CH_3CN . [PhTt^{tBu}]Tl (602 mg, 1.0 mmol) was added in small portions to the stirring solution of MnI_2 . TII precipitated immediately as a yellow solid. After stirring for 2 hr, the reaction mixture was filtered through Celite to remove TII and the solvent was removed in vacuo. Extracting the colorless residue with pentane/diethyl ether (v:v =

5:1) followed by filtering through Celite afforded a colorless solution. Removing the solvent in vacuo afforded a white solid (498 mg, 86%). Cooling a concentrated pentane solution to -30°C provided colorless crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 22.5 (br, C(CH₃)₃S), 10.0 (br), 7.5 (s), 6.6 (s). FTIR (KBr): 3058, 3040, 2958, 2894, 2858, 1456, 1426, 1402, 1366, 1260, 1163, 1069, 1024, 945, 899, 869, 751, 703, 582, 506. LIFDI-MS: calcd. for C₂₁H₃₈BMnIS₃ (M)⁺ 579.0658 *m/z*, found (M)⁺ 579.0652 *m/z* (100%). μ_{eff} (C₆D₆) = 5.9(1) μ_{B} .

[PhTt^{tBu}]CoI

Anhydrous CoI₂ (313 mg, 1.0 mmol) was dissolved in 50 mL of THF. [PhTt^{tBu}]Tl (602 mg, 1.0 mmol) was added in small portions resulting in precipitation of a yellow solid, TII. After stirring for 6 hr, the reaction mixture was filtered through Celite to separate TII. The solvent was then removed in vacuo affording a green solid (500 mg, 86%). Slow evaporation of a concentrated diethyl ether solution afforded green crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 14.1 (27H, br, C(CH₃)₃S), 9.0 (1H, s, *p*-(C₆H₅)B), 7.4 (2H, s, *m/o*-(C₆H₅)B). UV-vis (THF): λ_{max} (ε , M⁻¹ cm⁻¹) 314 (3600), 369 (4070), 665 (sh), 712 (1410), 986 (412). FTIR (KBr): 3061, 3037, 2964, 2894, 2861, 1456, 1423, 1396, 1366, 1260, 1160, 1024, 948, 899, 866, 748, 706, 576, 503. LIFDI-MS: calcd. for C₂₁H₃₈BCoIS₃ (M)⁺ 583.0610 *m/z*, found (M)⁺ 583.0637 *m/z* (100%). μ_{eff} (C₆D₆) = 4.58(3) μ_{B} .

[PhTt^{tBu}]Fe(PhenSQ)

Method A: A suspension of Tl(PhenSQ)³ (43 mg, 0.10 mmol) in 20 mL THF was added dropwise to a stirring solution of [PhTt^{tBu}]FeI (60 mg, 0.10 mmol) in 10 mL THF. The addition lasted for 30-40 min, during which time a yellow precipitate formed and the color of the solution changed from light yellow to dark greenish brown. The mixture was stirred for 2 additional hr. and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether (v:v = 1:1). Filtering the solution through Celite followed by removing the solvent in vacuo yielded a dark greenish brown solid (65 mg, 95%). Cooling a concentrated diethyl ether/pentane solution to -30°C provided yellow brown crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 115.6 (2H, br, C₁₄H₈O₂), 108.1 (2H, s, C₁₄H₈O₂), 20.4 (2H, s, *m*-(C₆H₅)B), 12.1 (2H, s, *o*-(C₆H₅)B), 11.4 (1H, s, *p*-(C₆H₅)B), -3.2 (27H, br, C(CH₃)₃S), -5.6 (2H, s, C₁₄H₈O₂), -13.0 (2H, s, C₁₄H₈O₂). UV-vis (THF): λ_{max} (ε , M⁻¹ cm⁻¹) 246 (28200), 268 (24900), 321 (5310), 401 (5230), 465 (sh), 496 (sh), 600 (868), 935 (539). FTIR (KBr): 3058, 3043, 2958, 2891, 2861, 1596, 1574, 1538, 1469, 1456, 1402, 1363, 1290, 1163, 1027, 951, 863, 757, 703, 576, 542. LIFDI-MS: calcd. for C₃₅H₄₆BFeO₂S₃ (M)⁺ 661.2109 *m/z*, found (M)⁺ 661.2100 *m/z* (100%). μ_{eff} (C₆D₆) = 4.65(2) μ_{B} .

Method B: 9,10-phenanthrenequinone (33 mg, 0.16 mmol) in 50 mL diethyl ether was added dropwise to a stirring solution of $[PhTt^{Hu}]Fe(PMe_3)$ (83 mg, 0.16 mmol) in 20 mL of pentane over approximately 1 hr., after which time the color of the solution changed from blue to dark greenish brown. The reaction mixture was stirred an additional hr. and the solvent was removed in vacuo. The solid residue was extracted with pentane and the solution was filtered through Celite. Removing the solvent provided a dark greenish brown solid (68 mg, 65%).

[PhTt^{tBu}]Mn(PhenSQ)

A suspension of Tl(PhenSQ) (86 mg, 0.21 mmol) in 30 mL THF was added dropwise to a stirring solution of [PhTt^{tBu}]MnI (116 mg, 0.20 mmol) in 15 mL THF over 40 mins, during which a yellow precipitate formed and the color of the solution changed from green to brown. The mixture was stirred

for 2 more hours and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether (v:v = 1:1). Filtering the solution through Celite followed by removing the solvent in vacuo yielded a brown solid (119 mg, 90%). Cooling a concentrated diethyl ether/pentane solution to -30°C provided brown crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 12.8 (br, C(CH₃)₃S), 9.4 (br), 7.8 (br), -25.1 (br), -29.7 (br). UV-vis (THF): λ_{max} (ε , M⁻¹ cm⁻¹) 257 (28300), 278 (31200), 310 (6130), 322 (8370), 408 (9020), 467 (sh), 500 (3350). FTIR (KBr): 3058, 2958, 2891, 2861, 1674, 1647, 1593, 1556, 1511, 1472, 1426, 1402, 1363, 1290, 1160, 1031, 954, 754, 710, 648, 580, 545. LIFDI-MS: calcd. for C₃₅H₄₆BMnO₂S₃ (M)⁺ 660.2140 *m/z*, found (M)⁺ 660.2155 *m/z* (100%). μ_{eff} (C₆D₆) = 5.01(6) μ_{B} .

[PhTt^{tBu}]Co(PhenSQ)

Method A: A suspension of Tl(PhenSQ) (74 mg, 0.18 mmol) in 30 mL THF was added dropwise to a stirring solution of [PhTt^{IBu}]CoI (100 mg, 0.17 mmol) in 15 mL THF over 40 min, during which a yellow precipitate formed and the color of the solution changed from green to orange-brown. The mixture was stirred for 2 more hours and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane/diethyl ether (v:v = 1:1). Filtering the solution through Celite followed by removing the solvent in vacuo yielded an orange-brown solid (102 mg, 89%). Cooling a concentrated diethyl ether/pentane solution to -30°C provided green brown crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 109.9 (2H, s, C₁₄H₈O₂), 101.4 (2H, s, C₁₄H₈O₂), 32.3 (2H, s, *m*-(C₆H₅)B), 17.3 (2H, s, *o*-(C₆H₅)B), 15.3 (1H, s, *p*-(C₆H₅)B), 2.6 (2H, s, C₁₄H₈O₂), -11.3 (2H, s, C₁₄H₈O₂), -21.8 (27H, br, C(CH₃)₃S). UV-vis (THF): λ_{max} (ϵ , M⁻¹ cm⁻¹) 257 (31800), 268 (32100), 393 (7830), 508 (7610), 683 (1310), 803 (1290). FTIR (KBr): 3061, 3046, 2958, 2922, 2891, 2864, 1671, 1590, 1574, 1469, 1447, 1390, 1363, 1341, 1299, 1260, 1160, 1108, 1036, 954, 869, 800, 751, 700, 663, 603, 566. LIFDI-MS: calcd. for C₃₅H₄₆BCoO₂S₃ (M)⁺ 664.2092 *m/z*, found (M)⁺ 664.2104 *m/z* (100%). μ_{eff} (C₆D₆) = 5.01(6) μ_{B} . Anal. Calcd. for C₃₅H₄₆BCoO₂S₃: %C, 63.24; %H, 6.98. Found: %C, 62.88; %H, 6.95.

Method B: 9, 10-phenanthrenequinone (33 mg, 0.16 mmol) in 50 mL diethyl ether was added dropwise to a stirring solution of $[PhTt^{IBu}]Co(PMe_3)$ (84 mg, 0.16 mmol) in 20 mL of pentane over approximately 1 hour, after which the color of the solution changed from pale green to orange-brown. The reaction mixture was stirred an additional hour and the solvent was removed in vacuo. The solid residue was extracted with pentane and the solution was filtered through Celite. Removing the solvent provided an orange-brown solid (73 mg, 70%).

[PhTt^{tBu}]Co(3,5-DBSQ)

A solution of Tl(3,5-DBSQ) (134 mg, 0.32 mmol) in 20 mL THF was added dropwise to a stirring solution of [PhTt^{tBu}]CoI (175 mg, 0.30 mmol) in 40 mL diethyl ether over 40 min, during which time a yellow precipitate formed and the color of the solution changed from green to dark reddish brown. The mixture was stirred for 2 more hours and filtered through Celite. Solvent was removed in vacuo and the residue was extracted with pentane. Filtering the solution through Celite followed by removing the solvent in vacuo yielded a dark reddish brown solid (182 mg, 90 %). Cooling a concentrated pentane/toluene solution to -30°C provided dark green brown crystals suitable for X-ray crystallography. ¹H NMR (C₆D₆): δ 75.4 (6H, br, BCH₂), 30.5 (1H, s, 4/6-DBSQ-H), 21.3 (2H, s, *m*-(C₆H₅)B), 12.9 (2H, s, *o*-(C₆H₅)B), 11.7 (1H, s, *p*-(C₆H₅)B), 3.6 (9H, s, 3/5-DBSQ-C(CH₃)₃), -2.1 (9H, s, 3/5-DBSQ-C(CH₃)₃), -11.8 (27H, br, C(CH₃)₃S). UV-vis (THF): λ_{max} (ε , M⁻¹ cm⁻¹) 298 (9940),

495 (4120), 784 (5470). FTIR (KBr): 3063, 3041, 2959, 2893, 2862, 1578, 1523, 1462, 1394, 1359, 1303, 1281, 1231, 1196, 1158, 1099, 1024, 983, 958, 870, 747, 704, 600, 572. LIFDI-MS: calcd. for $C_{35}H_{58}BCoO_2S_3$ (M)⁺ 676.3030 *m/z*, found (M)⁺ 676.3026 *m/z* (100%). μ_{eff} (C₆D₆) = 2.91(2) μ_{B} .

Reactivity of [PhTt^{tBu}]Co(3,5-DBSQ) with O₂

Procedure: Into a solution of [PhTt^{Bu}]Co(3,5-DBSQ) (50 mg, 0.074 mmol) in 15 mL of THF was bubbled dry O_2 for 3 min at room temperature. The solution was stirred for 16 hours, during which time the color of the solution changed from dark reddish brown to orange. The solution was concentrated to 2-3 mL in vacuo and 1M HCl (1 mL, 1.0 mmol) or Na₂EDTA (82 mg, 0.22 mmol) in 10 mL H₂O was added to liberate semiquinone-derived products. After stirring for 5 min, 15 mL of H_2O was added and the solution was extracted with ethyl ether (3 \times 25 mL). The organic layer was combined and dried with anhydrous MgSO₄. The products were obtained after removing ethyl ether in vacuo. The production of 3,5-di-tert-butyl muconic anhydride (an intradiol cleaving product) and 4,6-di-tert-butyl-2-phenyl-benzo[1,3,2]dioxaborole (a catechol derived phenylboronic ester) was confirmed by ¹H NMR, GC-MS (EI) and high resolution mass spectroscopy. An authentic sample of 4,6-di-tert-butyl-2-phenyl-benzo[1,3,2]dioxaborole was also prepared following the literature procedure.⁸ ¹H NMR spectroscopy was used to quantify the products (methyl *t*-butyl ether was the internal standard). 3,5-di-*tert*-butyl muconic anhydride (16%): ¹H NMR (CDCl₃) δ 6.43 (1H, d, J = 1.2 Hz, 4-H), 6.13 (1H, d, J = 1.2 Hz, 6-H), 1.26 (9H, s, tBu), 1.15 (9H, s, tBu). CI-MS: calcd. for $C_{14}H_{21}O_{3}$ 237.1491 (M + $\mathrm{H})^{+}$ m/z, found (M + $H)^+$ 237.1509 m/z. 4,6-di-*tert*-butyl-2-phenyl-benzo[1,3,2]dioxaborole (4%): ¹H NMR (CDCl₃) δ 8.11 (2H, dd J_1 = 8 Hz, $J_2 = 1.2$ Hz), 7.57 (1H, m), 7.49 (2H, m), 7.25 (1H, d, J = 2 Hz), 7.10 (1H, d, J = 2 Hz), 1.52 (9H, s), 1.37 (9H, s). EI-MS: calcd. for $C_{20}H_{25}O_2B$ (M)⁺ 308.1951 m/z, found (M)⁺ 308.1963 m/z.

Reactivity of $[PhTt^{tBu}]MX$ (M = Co, X = Cl, I; M = Fe, X = Cl) with 3,5-DBQ

and H₂O₂

Procedure: 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ, 22 mg, 0.10 mmol) and H₂O₂ (30% H₂O solution, 22.5 μ L, 0.22 mmol) was added to a stirring solution of [PhTt^{tBu}]CoX (X = Cl, I) or [PhTt^{tBu}]FeCl (0.10 mmol) in 15 mL THF. After 16 hours, 1M HCl (1 mL, 1.0 mmol) or EDTANa₂ (112 mg, 0.30 mmol) in 10 ml H₂O was added to liberate 3,5-DBQ-derived products. The solution was extracted with ethyl ether (3 × 25 mL). The organic layer was combined and dried with anhydrous MgSO₄. The products were obtained after removing ethyl ether in vacuo. The ¹H NMR spectrum showed that 4,6-di-*tert*-butyl-2-phenyl-benzo[1,3,2]dioxaborole was formed, but no 3,5-di-*tert*-butyl muconic anhydride was detected. These results indicate that muconic anhydride was not derived from simple oxidation of 3,5-DBQ by reactive oxygen species.

Reaction of $[PhTt^{tBu}]M(PhenSQ)$ (M = Fe, Co) with O₂ Monitored by UV-vis

Spectroscopy

Procedure: In a glovebox, [PhTt^{tBu}]M(PhenSQ) (2.0 mg, 0.0030 mmol) was dissolved in 10 mL toluene. 3 mL of the solution was transferred to a cryostat UV-vis cuvette charged with a magnetic

stirring bar. The cuvette was sealed with a rubber septum and brought out of the glovebox. With gentle stirring, the solution was exposed to a stream of dry O_2 gas at -90°C for 15 seconds. Spectra were collected every one minute until no spectral changes were observed at -90°C. The temperature was then raised to 0°C for 5 min for [PhTt^{tBu}]Fe(PhenSQ) or 20°C for 10 min for [PhTttBu]Co(PhenSQ) to monitor the timecourse of the thermal decay. After spectral changes ceased, the sample was cooled back to -90°C to collect the spectrum of the final products.

X-ray Crystallography

X-ray structural analyses for [PhTt^{tBu}]Fe(phenSQ), [PhTt^{tBu}]Co(phenSQ), [PhTt^{tBu}]CoI, [PhTt^{tBu}]MnI, [PhTt^{tBu}]Mn(phenSQ), and [PhTt^{tBu}]Co(3,5-DBSQ): Crystals were mounted using viscous oil onto plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II CCD diffractometer with graphite-monochromated Mo-K α radiation (λ =0.71073 Å). Unit cell parameters were obtained from 36 data frames, 0.3° w, from three different sections of the Ewald sphere. No symmetry higher than triclinic was observed for [PhTt^{tBu}]Fe(phenSQ). The systematic absences in the diffraction data are consistent with Cc and C2/c for [PhTt^{iBu}]Mn(phenSQ), and, uniquely, for $P2_1/n$ for [PhTt^{tBu}]Co(phenSQ), for $P2_1/c$ for [PhTt^{tBu}]CoI, and for Pbca for [PhTt^{tBu}]MnI. For [PhTt^{tBu}]Fe(phenSQ) and [PhTt^{tBu}]Mn(phenSQ), solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. No symmetry higher than triclinic was observed for [PhTt^{tBu}]Co(3,5-DBSQ), and solution in the centrosymmetric space group option yielded computationally stable and chemically stable results of refinement. One molecule of pentane was found cocrystallized in the asymmetric unit of [PhTt^{tBu}]Co(3,5-DBSQ). The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.⁷ The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{ea} of the attached atom. Structure factors are contained in the SHELXTL 6.12 program library.⁷ Structural information has been deposited with the Cambridge Structural Crystallographic Centre under depositary numbers CCDC 969713-969717.



Figure S1. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{tBu}]FeI.



Figure S2. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{tBu}]CoI.



Figure S3. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{Bu}]MnI.



Figure S4. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{iBu}]Fe(phenSQ). Insets are calculated (top) and experimental (bottom) isotope distribution patterns.



Figure S5. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{tBu}]Mn(phenSQ). Insets are calculated (top) and experimental (bottom) isotope distribution patterns.



Figure S6. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{iBu}]Co(phenSQ). Insets are calculated (top) and experimental (bottom) isotope distribution patterns.



Figure S7. Calculated (top) and experimental (bottom) high resolution LIFDI mass spectra of [PhTt^{tBu}]Co(3,5-DBSQ). Insets are calculated (top) and experimental (bottom) isotope distribution patterns.



Figure S8. ¹H NMR spectrum of [PhTt^{Bu}]FeI recorded in *C₆D₆.



Figure S9. ¹H NMR spectrum of [PhTt^{tBu}]CoI recorded in $*C_6D_6$.



Figure S10. ¹H NMR spectrum of [PhTt^{tBu}]MnI recorded in $*C_6D_6$.



Figure S11. ¹H NMR spectrum of [PhTt^{iBu}]Fe(phenSQ) recorded in $*C_6D_6$. Insets are proton signals in the low-field region, whose integrations are not accurate due to paramagnetism.



Figure S12. ¹H NMR spectrum of [PhTt^{tBu}]Mn(phenSQ) recorded in $*C_6D_6$.



Figure S13. ¹H NMR spectrum of [PhTt^{tBu}]Co(phenSQ) recorded in *C₆D₆.



Figure S14. ¹H NMR spectrum of [PhTt^{tBu}]Co(3,5-DBSQ) recorded in $*C_6D_6$.



Figure S15. Comparison of the IR spectra of [PhTt^{tBu}]FeI (top) and [PhTt^{tBu}]Fe(phenSQ) (bottom).



Figure S16. Comparison of the IR spectra of [PhTt^{tBu}]MnI (top) and [PhTt^{tBu}]Mn(phenSQ) (bottom).



Figure S17. Comparison of the IR spectra of [PhTt^{tBu}]CoI (top) and [PhTt^{tBu}]Co(phenSQ) (bottom).



Figure S18. Comparison of the IR spectra of [PhTt^{tBu}]CoI (top) and [PhTt^{tBu}]Co(3,5-DBSQ) (bottom).

Compound	LMnI	LCoI	LFe(phenSQ)	LMn(phenSQ)	LCo(phenSQ)	LCo(3,5-DBSQ)
Empirical	$C_{21}H_{38}BIMnS_3\\$	$C_{21}H_{38}BIMnS_3\\$	$\mathrm{C_{35}H_{46}BFeO_2S_3}$	$C_{35}H_{46}BMnO_2S_3$	$\mathrm{C_{35}H_{46}BCoO_2S_3}$	$\mathrm{C}_{40}\mathrm{H}_{70}\mathrm{BCoO}_2\mathrm{S}_3$
Formula						
Formula	579.34	583.33	661.56	660.65	664.64	748.88
Weight						
Temperature,	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
К						
Wavelength,	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Å						
Crystal	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
System						
Space Group	Pbca	$P2_{1}/c$	PĪ	C2/c	P2(1)/n	PĪ
<i>a</i> , Å	10.215(3)	12.297(1)	10.245(1)	22.616(6)	10.404(1)	12.267(1)
<i>b</i> , Å	14.928(4)	9.537(1)	11.922(1)	11.592(3)	16.494(2)	12.743(1)
<i>c</i> , Å	35.622(8)	23.054(3)	14.993(2)	26.845(7)	20.710(2)	15.234(1)
α, deg	90	90	74.462(2)	90	90	96.260(1)
β , deg	90	90.592(2)	80.159(2)	95.602(6)	103.018(2)	113.471(1)
γ, deg	90	90	78.808(2)	90	90	98.383(1)
<i>V</i> , Å ³	5432(2)	2704(1)	1717.0(3)	7004(3)	3463(1)	2124.0(1)
Ζ	8	4	2	8	4	2
Density,	1.417	1.433	1.280	1.253	1.275	1.171
Mg/m ³						
F(000)	2360	1188	702	2800	1408	812
Crystal Size,	0.36 imes 0.25 imes	0.25 $ imes$ 0.19 $ imes$	0.27 $ imes$ 0.22 $ imes$	0.37 $ imes$ 0.21 $ imes$	0.68 $ imes$ 0.42 $ imes$	0.57 $ imes$ 0.37 $ imes$
mm ³	0.25 mm	0.13 mm	0.08 mm	0.18 mm	0.30 mm	0.15 mm
Theta Range	2.287 to 27.685	1.656 to 27.608	1.80 to 27.75	1.524 to 27.669	1.59 to 27.48	1.483 to 27.693
for Data						
Collection,						
deg						
Final R	R1 = 0.0456,	$R_1 = 0.0274,$	R1 = 0.0415,	$R_1 = 0.0585,$	$R_1 = 0.0277,$	$R_1 = 0.0389,$
indices	wR2 = 0.0885	wR2 = 0.0575	wR2 = 0.1035	wR2 = 0.1179	wR2 = 0.0747	wR2 = 0.0883
[I>2sigma(I)]						

Table S1. Crystallographic data for complexes LMnI, LCoI, LFe(phenSQ), LMn(phenSQ), LCo(phenSQ), LCo(3,5-DBSQ) (L = [PhTt^{tBu}]).



Figure S19. Molecular structures of [PhTt^{tBu}]MnI (left) and [PhTt^{tBu}]CoI (right) with thermal ellipsoids at the 30% probability level. H-atoms are omitted for clarity.



Figure S20. Molecular structures of [PhTt^{tBu}]M(phenSQ) and [PhTt^{tBu}]Co(3,5-DBSQ) with thermal ellipsoids at the 30% probability level. H-atoms are omitted for clarity. Top (left): [PhTt^{tBu}]Fe(phenSQ); Top (right): [PhTt^{tBu}]Mn(phenSQ); Bottom (left): [PhTt^{tBu}]Co(phenSQ); Bottom (right): [PhTt^{tBu}]Co(3,5-DBSQ)·(C₅H₁₂) Pentane not shown. Key metric parameters for M^{II}-phenSQ complexes are contained in Table 1. Key bond lengths for [PhTt^{tBu}]Co(3,5-DBSQ): Co1–O1 1.874(1), Co1–O2 1.893(1), O1–C22, 1.309(2), O2–C23 1.318(2), C22–C23 1.422(3).



Figure S21. Spacefilling models of the molecular structures of: $[PhTt^{tBu}]Fe(phenSQ)$ (upper left); $[PhTt^{tBu}]Mn(phenSQ)$ (upper right); $[PhTt^{tBu}]Co(phenSQ)$ (lower left); $[PhTt^{tBu}]Co(3,5-DBSQ) \cdot (C_5H_{12})$ (pentane is not shown) (lower right).



Figure S22. Cyclic voltammograms of [PhTt^{tBu}]M(phenSQ) (M = Fe (red), Mn (green), Co (blue)) and [PhTt^{tBu}]Co(3,5-DBSQ) (purple) measured in THF with 0.1M NBu₄PF₆ as the supporting electrolyte. Scan rates: Fe(phenSQ), 300 mV/s; Mn(phenSQ), Co(phenSQ) and Co(3,5-DBSQ), 100 mV/s. Decamethylferrocene/ferrocenium (Me₁₀Fc^{+/0}) were used as the internal reference. All potentials were referred to Fc^{+/0} based on a 0.447 V separation between the potentials of Me₁₀Fc^{+/0} and Fc^{+/0} under the same experimental conditions.



Figure S23. High resolution CI (methane) mass spectra of the muconic anhydride derived from the reaction of [PhTt^{tBu}]Co(3,5-DBSQ) with O₂. Top: calculated spectrum of muconic anhydride, $(M + H^+) m/z = 237.1491$; Bottom: experimental spectrum, $(M + H^+) m/z = 237.1509$.



Figure S24. ¹H NMR spectrum of the products from the reaction of [PhTt^{tBu}]Co(3,5-DBSQ) with O₂. The spectrum was recorded in CDCl₃. Proton signals from the muconic anhydride are labeled.



Figure S25. High resolution EI-MS of 4,6-di-*tert*-butyl-2-phenyl-benzo[1,3,2]dioxaborole derived from the reaction of [PhTt^{tBu}]Co(3,5-DBSQ) with O₂. Top: calculated spectrum, $(M)^+$ m/z = 308.1951; Bottom: experimental spectrum, $(M)^+$ m/z = 308.1963.



4,6-di-tert-butyl-2-phenyl-benzo[1,3,2]dioxaborole recorded in CDCl₃.



Figure S27. Low-field region of the ¹H NMR spectrum of 4,6-di-*tert*-butyl-2-phenyl-benzo[1,3,2]dioxaborole derived from the reaction of [PhTt^{tBu}]Co(3,5-DBSQ) with O₂. The spectrum was recorded in CDCl₃.



Figure S28. Electronic spectral changes during the reactions of $[PhTt^{tBu}]Co(phenSQ)$ with O₂ at -90°C in toluene. The spectra of all species were collected at -90°C. The spectrum of the product was obtained by warming the system to 20°C for 10 min and then cooling back to -90°C for 15 min.

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