

Electronic Supporting Information for:

Gauging electronic dissymmetry in bis-chelates of titanium(IV) using sterically and electronically variable 2,2'-biphenoxides

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I. Preparation and Characterization of Compounds

General procedures. Chloroform and methylene chloride were dried over 4 Å molecular sieves, followed by CaH₂. Benzene and toluene were dried over sodium, and ether and tetrahydrofuran over sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedure as their protio analogues, and stored in the drybox prior to use. 3,3',5,5'-Tetramethyl-2,2'-biphenol was purchased from Strem Chemicals; the other 3,3',5,5'-tetrasubstituted biphenols C₁₂H₄Br₄(OH)₂,^{S1} C₁₂H₄(NO₂)₄(OH)₂,^{S2} and C₁₂H₄(^tBu)₄(OH)₂^{S3} were prepared by published routes, as were the bis(diketonate) complex (Bob)Ti(O^{*i*}Pr)₂^{S4} and the hydroxamate complexes (Hox)Ti(O^{*i*}Pr)₂ and (Hob)Ti(O^{*i*}Pr)₂.^{S5} All other reagents were commercially available and used without further purification. NMR spectra were measured on a Varian VXR-300 or VXR-500 spectrometer. Chemical shifts for ¹H and ¹³C{¹H} spectra are reported in ppm downfield of TMS, referenced to the chemical shifts of the solvent residuals. All NMR spectra were taken at 20 °C unless otherwise indicated. Infrared spectra were recorded on KBr plates on a Perkin-Elmer PARAGON 1000 FT-IR or a Nicolet NEXUS 670 FT-IR spectrometer. Mass spectra were obtained on a JEOL LMS-AX505HA mass spectrometer using the FAB ionization mode and 3-nitrobenzyl alcohol or nitrophenyl octyl ether as a matrix. Peaks reported are the mass number of the most intense peak of the isotope envelopes. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

(Bob)Ti(O₂C₁₂H₄Br₄). In the drybox, (Bob)Ti(O^{*i*}Pr)₂ (0.0715 g, 0.107 mmol), 3,3',5,5'-tetrabromo-2,2'-dihydroxybiphenyl (0.0542 g, 0.108 mmol), 5 mL of CHCl₃ and a magnetic stirbar were charged into a scintillation vial. The mixture was stirred for 10 min, and then hexanes (3 mL) was added. The resulting orange precipitate was filtered, washed with 2 × 1 mL hexanes and dried *in vacuo* for 1 h. Yield: 0.0831 g (74%). ¹H NMR (CD₂Cl₂): δ 2.42 (s, 6H,

tolyl CH_3), 3.31 (d, 14 Hz, 2H, CHH'), 4.11 (d, 14 Hz, 2H, CHH'), 5.66 (s, 2H, COCHCO), 7.16 (d, 7.5 Hz, 2H, 3-H biphenyl), 7.16 (td, 8, 2.5 Hz, 2H, 4-H biphenyl), 7.21 (d, 8 Hz, 4H, Tol 3,5-H), 7.43 (d, 7.5 Hz, 2H, 6-H biphenyl), 7.44 (d, 8 Hz, 4H, Tol 2,6-H), 7.45 (d, 2.5 Hz, 2H, 6,6'-H biphenolate), 7.50 (td, 8, 2.5 Hz, 2H, 5-H biphenyl), 7.72 (d, 2.5 Hz, 2H, 4,4'-H biphenolate).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 22.04 (tolyl CH_3), 46.00 (CH_2), 104.53 (COCHCO), 113.38, 114.16, 127.88, 129.02, 129.09, 129.54, 129.68, 130.10, 131.50, 133.11, 133.64, 134.80, 136.68, 140.80, 145.01, 160.15, 182.06 (CO), 191.69 (CO). IR (cm^{-1}): 2916 (w), 1608 (w), 1586 (w), 1550 (m), 1515 (s), 1498 (s), 1435 (m), 1388 (m), 1350 (m), 1322 (m), 1297 (w), 1287 (w), 1262 (m), 1184 (m), 1156 (w), 1052 (w), 984 (w), 863 (w), 767 (w), 720 (w). FABMS: m/z 1044 (M^+ , $^{79}Br_4$ isotopomer). Anal. Calcd for $C_{46}H_{32}Br_4O_6Ti$: C, 52.71; H, 3.08. Found: C, 52.72; H, 3.35.

(Hox)Ti(O₂C₁₂H₄Br₄). This compound was prepared by the procedure described above using (Hox)Ti(O^{*i*}Pr)₂ (0.0727 g, 0.147 mmol) and 3,3',5,5'-tetrabromo-2,2'-dihydroxybiphenyl (0.0745 g, 0.148 mmol). After stirring for 10 min, the resulting yellow precipitate was filtered and redissolved in ~15 mL of hot CH_2Cl_2 . The product precipitated as a yellow solid on standing at 10 °C overnight. Isolation by filtration, washing with 2 × 1 mL hexanes and drying *in vacuo* for 1 h yielded 0.0292 g (23%) of the product. 1H NMR (CD_2Cl_2): δ 2.85 (s, 6H, NCH_3), 3.51 (d, 16 Hz, 2H, CHH'), 4.19 (d, 16 Hz, 2H, CHH'), 7.29 (m, 2H, Ar-H biphenyl), 7.30 (d, 2.5 Hz, 2H, 6-H biphenol), 7.49 (m, 6H, Ar-H biphenyl), 7.60 (d, 2.5 Hz, 2H, 4-H biphenol). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 34.96 (NCH_3), 38.62 (CH_2), 113.09, 114.29, 121.05, 128.58, 129.05, 130.32, 132.68, 133.12, 134.55, 135.09, 139.52, 158.40, 165.69 (CO). IR (cm^{-1}): 3061 (w), 3015 (w), 2989 (w), 2932 (w), 1582 (s, ν_{CO}), 1475 (w), 1463 (w), 1437 (s), 1413 (s), 1392 (s), 1248 (s), 1056 (m), 868 (w), 856 (m), 840 (w), 824 (w), 769 (m), 756 (m), 743 (m), 717 (m). FABMS: m/z 870 (M^+ ,

$^{79}\text{Br}_4$ isotopomer). Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{Br}_4\text{N}_2\text{O}_6\text{Ti}$: C, 41.23; H, 2.54; N, 3.21. Found: C, 41.45; H, 2.70; N, 3.27.

(Hob)Ti(O₂C₁₂H₄Br₄). This compound was prepared by the procedure described above using (Hob)Ti(O^{*i*}Pr)₂ (0.0608 g, 0.105 mmol) and 3,3',5,5'-tetrabromo-2,2'-dihydroxybiphenyl (0.0530 g, 0.106 mmol). After stirring for 30 min, the resulting orange precipitate was filtered, washed with 2 × 1 mL hexanes and dried *in vacuo* for 1 h. Yield: 0.0727 g (72%). ¹H NMR (CD₂Cl₂): δ 2.39 (s, 3H, tolyl CH₃), 2.65 (s, 3H, NCH₃), 3.37 (d, 15 Hz, 1H, CH_cH_dCOCHCOTol), 3.58 (d, 15 Hz, 1H, CH_aH_bCON(CH₃)O), 4.11 (d, 15 Hz, 1H, CH_cH_dCOCHCOTol), 4.20 (d, 15 Hz, 1H, CH_aH_bCON(CH₃)O), 5.88 (s, 1H, COCHCO), 7.20 (d, 9 Hz, 2H, Tol 3,5-H), 7.36 (d, 2.5 Hz, 1H, 6-H biphenolate), 7.39 (d, 2.5 Hz, 1H, 6'-H biphenolate), 7.41 (m, 8H, Ar-H biphenyl), 7.51 (d, 9 Hz, 2H, Tol 2,6-H), 7.64 (d, 2.5 Hz, 1H, 4-H biphenolate), 7.69 (d, 2.5 Hz, 1H, 4'-H biphenolate). ¹³C{¹H} NMR (CD₂Cl₂): δ 21.97 (tolyl CH₃), 34.98 (NCH₃), 38.78 (CH₂ hydroxamate), 46.06 (CH₂ diketonate), 103.79 (COCHCO), 112.94, 113.57, 114.08, 114.30, 128.37, 128.41, 128.77, 128.87, 128.90, 129.11, 129.46, 129.74, 130.08, 130.46, 131.67, 132.72, 132.89, 132.95, 134.05, 134.43, 134.99, 136.98, 139.76, 140.50, 144.80, 159.01, 159.35, 164.56 (CO hydroxamate), 181.53 (CO diketonate), 194.13 (CO diketonate). IR (cm⁻¹): 3056 (w), 3020 (w), 2942 (w), 2916 (w), 1583 (m, ν_{CO}), 1549 (m), 1520 (s), 1496 (s), 1436 (s), 1389 (s), 1350 (m), 1332 (m), 1291 (w), 1263 (s), 1186 (m), 1161 (w), 1096 (w), 1052 (m), 984 (w), 886 (w), 860 (m), 824 (m), 766 (m), 754 (w), 741 (w), 718 (m). FABMS: *m/z* 957 (M⁺, $^{79}\text{Br}_4$ isotopomer). Anal. Calcd for $\text{C}_{38}\text{H}_{27}\text{Br}_4\text{NO}_6\text{Ti}$: C, 47.49; H, 2.83; N, 1.46. Found: C, 47.24; H, 3.05; N, 1.42.

(Bob)Ti(O₂C₁₂H₄[CH₃]₄). In the drybox, (Bob)Ti(O^{*i*}Pr)₂ (0.1000 g, 0.1504 mmol) was charged into a scintillation vial with a magnetic bar and dissolved in 10 mL of CH₂Cl₂. 3,3',5,5'-

Tetramethyl-2,2'-dihydroxybiphenyl (0.0363 g, 0.150 mmol) was weighed into a separate vial, dissolved in 5 mL of CH_2Cl_2 and added dropwise with vigorous stirring to the $(\text{Bob})\text{Ti}(\text{O}^i\text{Pr})_2$ solution. The resulting pale red mixture was stirred for 44 h at room temperature and the solvent evaporated *in vacuo* to yield a sticky red solid. This solid was crushed with hexanes (15 mL), filtered, washed with hexanes (2×5 mL) and dried *in vacuo* for 1 h. Yield: 0.0972 g (82%). ^1H NMR (CDCl_3): δ 2.14 (s, 6H, biphenolate CH_3), 2.38 (s, 6H, biphenolate CH_3), 2.41 (s, 6H, tolyl CH_3), 3.25 (d, 13 Hz, 2H, CHH'), 4.03 (d, 13 Hz, 2H, CHH'), 5.54 (s, 2H, COCHCO), 7.00 (s, 2H, 4,4'-H biphenolate), 7.09 (s, 2H, 6,6'-H biphenolate), 7.14 (d, 8 Hz, 4H, Tol 3,5-H), 7.18 (m, 4H, biphenyl), 7.41 (m, 6H, Tol 2,6-H and biphenyl ArH), 7.50 (t, 8 Hz, 2H, 4- or 5-H biphenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 17.44 (biphenolate CH_3), 21.16 (biphenolate CH_3), 21.88 (tolyl CH_3), 46.10 (CH_2), 102.83 (COCHCO), 124.51, 127.14, 127.26, 128.64, 129.02, 129.29, 129.64, 129.77, 130.45, 132.13, 133.44, 136.81, 140.57, 143.21, 161.10, 181.05 (CO), 190.92 (CO). IR (nujol mull, cm^{-1}): 1653 (w), 1588 (m), 1554 (m), 1499 (m), 1323 (w), 1248 (w), 1496 (w) 1419 (m), 1184 (w), 1160 (m), 982 (m), 833 (m), 744 (m). FABMS: m/z 788 (M^+). Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{O}_6\text{Ti}$: C, 76.14; H, 5.62. Found: C, 74.34; H, 6.08.

(Hox)Ti(O₂C₁₂H₄[CH₃]₄). This compound was prepared by the procedure described above for $(\text{Bob})\text{Ti}(\text{O}_2\text{C}_{12}\text{H}_4[\text{CH}_3]_4)$, using $(\text{Hox})\text{Ti}(\text{O}^i\text{Pr})_2$ (0.1000 g, 0.2031 mmol) and 3,3',5,5'-tetramethyl-2,2'-dihydroxybiphenyl (0.0492 g, 0.203 mmol). After stirring for 2 h, the resulting yellow cloudy suspension was stripped down *in vacuo* to yield a crude yellow solid. This solid was crushed with hexanes (15 mL), filtered, washed with hexanes (2×5 mL) and dried *in vacuo* for 1 h. Yield: 0.1105 g (88%). The complex is only sparingly soluble in chlorinated solvents and insoluble in other solvents. ^1H NMR (CDCl_3): δ 2.24 (s, 6H, CH_3 biphenolate), 2.26 (s, 6H, CH_3 biphenolate), 2.77 (s, 6H, NCH_3), 3.41 (d, 16 Hz, 2H, CHH'), 4.08 (d, 16 Hz, 2H, CHH'),

6.87 (d, 2 Hz, 2H, biphenolate ArH), 6.94 (d, 2 Hz, 2H, biphenolate ArH), 7.25 (m, 2H, biphenyl ArH), 7.42 (m, 4H, biphenyl ArH), 7.49 (m, 2H, biphenyl ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 17.13 (CH_3 biphenolate), 21.00 (CH_3 biphenolate), 34.48 (NCH_3), 38.03 (CH_2), 125.38, 127.01, 127.81, 128.43, 129.04, 129.66, 129.91, 130.13, 133.38, 134.40, 139.32, 158.56, 164.16 (CO). IR (nujol mull, cm^{-1}): 1588 (s, ν_{CO}), 1419 (s), 1255 (s), 1211 (s), 1162 (w), 1128 (m), 994 (w), 857 (m), 829 (s), 778 (m), 756 (s), 746 (s), 727 (m), 667 (m), 639 (w), 586 (w). FABMS: m/z 615 ($\text{M}+\text{H}$)⁺. Anal. Calcd for $\text{C}_{34}\text{H}_{34}\text{N}_2\text{O}_6\text{Ti}$: C, 66.45; H, 5.58; N, 4.56. Found: C, 66.70; H, 5.44; N, 4.40.

(Hob)Ti(O₂C₁₂H₄[CH₃]₄). This compound was prepared by the procedure described above, using (Hob)Ti(OⁱPr)₂ (0.1000 g, 0.1725 mmol) and 3,3',5,5'-tetramethyl-2,2'-dihydroxybiphenyl (0.0418 g, 0.172 mmol). After stirring for 14 h, the solvent was evaporated from the orange solution and the orange residue was dried *in vacuo* for 1 h. The crude solid was stirred with hexanes (15 mL), filtered, washed with hexanes (2 × 5 mL) and dried *in vacuo* for 1 h. Yield: 0.1072 g (89%). ^1H NMR (CDCl_3): δ 2.05 (s, 3H, biphenolate CH_3), 2.29 (s, 3H, biphenolate CH_3), 2.30 (s, 3H, biphenolate CH_3), 2.34 (s, 3H, biphenolate CH_3), 2.39 (s, 3H, tolyl CH_3), 2.57 (s, 3H, NCH_3), 3.25 (d, 15 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 3.47 (d, 15 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 4.02 (d, 15 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 4.07 (d, 15 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 5.71 (s, 1H, COCHCO), 6.90 (s, br, 1H, 6-H biphenolate), 6.97 (s, br, 1H, 6'-H biphenolate), 6.99 (s, br, 1H, 4-H biphenolate), 7.03 (s, br, 1H, 4'-H biphenolate), 7.14 (d, 8 Hz, 2H, Tol 3,5-H), 7.33 (m, 6H, biphenyl ArH), 7.41 (d, 8 Hz, 2H, Tol 2,6-H), 7.47 (m, 2H, biphenyl ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 17.02 (CH_3 biphenolate), 17.66 (CH_3 biphenolate), 21.08 (tolyl CH_3), 21.82 (CH_3 biphenolate), 27.12 (CH_3 biphenolate), 34.52 (NCH_3), 38.09 (CH_2 hydroxamate), 45.98 (CH_2 diketonate), 102.27 (COCHCO), 125.03, 125.07, 126.83, 127.42,

127.59, 127.62, 128.19, 128.31, 128.41, 129.07, 129.11, 129.18, 129.63, 129.79, 129.86, 129.87, 129.96, 130.47, 132.56, 132.96, 133.97, 134.00, 137.28, 139.62, 140.20, 143.06, 159.65 (biphenolate CO), 159.75 (biphenolate CO), 163.17, (CO hydroxamate), 181.00 (CO diketonate), 192.41 (CO diketonate). IR (nujol mull, cm^{-1}): 1586 (s, ν_{CO}), 1555 (m), 1518 (s), 1255 (s), 1230 (m), 1185 (w), 1161 (m), 1095 (w), 981 (m), 836 (s), 753 (s) 744 (s), 721 (s), 624 (w). FABMS: m/z 702 (M+H)⁺. Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{NO}_6\text{Ti}$: C, 71.90; H, 5.60; N, 2.00. Found: C, 72.00; H, 5.60; N, 2.05.

(Bob)Ti(O₂C₁₂H₄[NO₂]₄). This compound was prepared by the procedure described for the tetrabromo compound using (Bob)Ti(OⁱPr)₂ (0.0611 g, 0.092 mmol) and 3,3',5,5'-tetranitro-2,2'-dihydroxybiphenyl (0.0339 g, 0.093 mmol). After stirring for 5 min, hexanes (3 mL) was added. The resulting yellow precipitate was filtered, washed with 2 × 1 mL of hexanes and dried *in vacuo* for 1 h. Yield: 56% (0.0468 g). ¹H NMR (CD₂Cl₂): δ 2.43 (s, 6H, tolyl CH₃), 3.36 (d, 14 Hz, 2H, CHH'), 4.16 (d, 14 Hz, 2H, CHH'), 5.74 (s, 2H, COCHCO), 7.21 (d, 7 Hz, 2H, 3-H biphenyl), 7.21 (d, 9 Hz, 4H, Tol 3,5-H), 7.29 (d, 9 Hz, 4H, Tol 2,6-H), 7.44 (d, 7 Hz, 2H, 6-H biphenyl), 7.52 (m, 4H, 4-, 5-H biphenyl), 8.52 (d, 2.5 Hz, 2H, 6,6'-H biphenolate), 8.86 (d, 2.5 Hz, 2H, 4,4'-H biphenolate). ¹³C{¹H} NMR (CD₂Cl₂): δ 22.15 (tolyl CH₃), 45.58 (CH₂), 106.21 (COCHCO), 122.28, 128.21, 128.92, 129.37, 130.07, 130.13, 130.53, 130.65, 130.85, 133.81, 136.10, 139.14, 140.33, 140.65, 146.37, 162.00, 183.41 (CO), 191.83 (CO). IR (cm^{-1}): 3085 (w), 2925 (w), 1579 (m), 1538 (s), 1511 (s), 1422 (m), 1336 (s), 1299 (m), 1284 (m), 1185 (m), 1092 (m), 984 (m), 951 (w), 848 (m), 834 (m), 790 (m), 745 (m), 718 (w). FABMS: m/z 913 (M+H)⁺. Anal. Calcd for $\text{C}_{46}\text{H}_{32}\text{N}_4\text{O}_{14}\text{Ti}$: C, 60.54; H, 3.53; N, 6.14. Found: C, 60.46; H, 3.60; N, 6.14.

(Hox)Ti(O₂C₁₂H₄[NO₂]₄). This compound was prepared by the procedure described above using (Hox)Ti(OⁱPr)₂ (0.0686 g, 0.139 mmol) and 3,3',5,5'-tetranitro-2,2'-

dihydroxybiphenyl (0.0514 g, 0.140 mmol). After stirring for 5 min, the resulting yellow precipitate was filtered, washed with 2×1 mL of hexanes and dried *in vacuo* for 1 h. Yield: 0.0873 g (85%). ^1H NMR (CD_2Cl_2): δ 2.82 (s, 6H, NCH_3), 3.57 (d, 16 Hz, 2H, CHH'), 4.21 (d, 16 Hz, 2H, CHH'), 7.30 (m, 2H, biphenyl ArH), 7.50 (m, 6H, biphenyl ArH), 8.39 (d, 2.5 Hz, 2H, 6,6'-H biphenolate), 8.69 (d, 2.5 Hz, 2H, 4,4'-H biphenolate). The compound was too insoluble for ^{13}C NMR analysis. IR (cm^{-1}): 3082 (w), 2916 (w), 1592 (m), 1535 (s), 1520 (s), 1462 (m), 1424 (m), 1346 (s), 1270 (m), 1093 (w), 953 (m), 912 (m), 850 (m), 824 (w), 744 (m). FABMS: m/z 739 ($\text{M}+\text{H}$) $^+$. Anal. Calcd for $\text{C}_{30}\text{H}_{22}\text{N}_6\text{O}_{14}\text{Ti}$: C, 48.80; H, 3.00; N, 11.38. Found: C, 48.70; H, 3.56; N, 11.47.

(Hob)Ti(O₂C₁₂H₄[NO₂]₄). This compound was prepared by the procedure described above using (Hob)Ti(OⁱPr)₂ (0.0525 g, 0.090 mmol) and 3,3',5,5'-tetranitro-2,2'-dihydroxybiphenyl (0.0334 g, 0.091 mmol). After stirring for 5 min, hexanes (10 mL) was added. The resulting yellow precipitate was filtered, washed with 2×1 mL of hexanes and dried *in vacuo* for 1h. Yield: 0.0358 g (48%). ^1H NMR (CD_2Cl_2): δ 2.41 (s, 3H, tolyl CH_3), 2.61 (s, 3H, NCH_3), 3.41 (d, 15.5 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 3.61 (d, 15.5 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 4.12 (d, 15.5 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 4.25 (d, 15.5 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 5.95 (s, 1H, COCHCO), 7.23 (d, 8.5 Hz, 2H, Tol 3,5-H), 7.31 (td, 7.5, 1.5 Hz, 1H, 4- or 4'-H biphenyl), 7.33 (d, 7.5 Hz, 1H, 3- or 3'-H biphenyl), 7.37 (d, 8.5 Hz, 2H, Tol 2,6-H), 7.41 (d, 7.5 Hz, 1H, 3- or 3'-H biphenyl), 7.48 (td, 7.5, 1.5 Hz, 2H, 5- and 5'-H biphenyl), 7.52 (m, 2H, Ar-H biphenyl), 7.57 (dd, 7.5, 1.5 Hz, 1H, 6- or 6'-H biphenyl), 8.42 (d, 3 Hz, 1H, 6-H biphenolate), 8.48 (d, 3 Hz, 1H, 6'-H biphenolate), 8.72 (d, 3 Hz, 1H, 4-H biphenolate), 8.86 (d, 3 Hz, 1H, 4'-H biphenolate). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 22.09 (tolyl CH_3), 34.86 (NCH_3), 39.02 (CH_2 hydroxamate), 45.77 (CH_2 diketonate), 105.54 (COCHCO), 122.07,

122.62, 128.71, 128.74, 129.14, 129.20, 129.95, 130.10, 130.16, 130.21, 130.35, 130.49, 130.78, 131.98, 133.56, 134.19, 134.80, 135.25, 136.49, 139.35, 139.87, 140.09, 140.32, 140.81, 145.99, 146.07, 160.57, 161.89, 165.26 (CO hydroxamate), 182.61 (CO diketonate), 194.85 (CO diketonate). IR (cm⁻¹): 3085 (w), 1579 (m), 1536 (s), 1519 (s), 1498 (m), 1460 (m), 1422 (m), 1337 (s), 1269 (m), 1186 (w), 1092 (m), 986 (w), 952 (w), 913 (w), 850 (m), 835 (m), 744 (m), 708 (m), 668 (m). FABMS: *m/z* 826 (M+H)⁺. Anal. Calcd for C₃₈H₂₇N₅O₁₄Ti: C, 55.29; H, 3.30; N, 8.48. Found: C, 54.67; H, 3.71; N, 6.51.

(Bob)Ti(O₂C₁₂H₄Bu₄). In the drybox, (Bob)Ti(O^{*i*}Pr)₂ (0.0710 g, 0.106 mmol), 3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (0.0444 g, 0.108 mmol), 5 mL toluene and a magnetic stirbar were added into a 25 mL round bottom flask, which was then sealed with a rubber septum. The flask was taken out of the drybox and connected to a condenser topped with a nitrogen-flushed tee vented to a bubbler. The mixture was heated with stirring in a 108 °C oil bath overnight, yielding a clear brown solution. The toluene was evaporated and the brown residue was redissolved in methylene chloride and purified by column chromatography on silica gel using 4:1 hexanes/ethyl acetate as eluent. The solvent was evaporated from the eluate and the solid suspended in 2 mL of hexanes. After stirring the suspension for 5 min, the brown solid was filtered, washed with 2 × 1 mL of hexanes and dried *in vacuo* for 1 h to yield 12.0 mg of the biphenoxide complex (12%). ¹H NMR (CD₂Cl₂): δ 1.30 (s, 18H, C(CH₃)₃), 1.38 (s, 18H, C(CH₃)₃), 2.37 (s, 6H, tolyl CH₃), 3.21 (d, 14 Hz, 2H, CHH'), 4.07 (d, 14 Hz, 2H, CHH'), 5.55 (s, 2H, COCHCO), 7.08 (dd, 7.5, 1.5 Hz, 2H, 3-H biphenyl), 7.09 (d, 8 Hz, 4H, Tol 3,5-H), 7.13 (td, 7.5, 1.5 Hz, 2H, 4-H biphenyl), 7.15 (d, 2.5 Hz, 2H, 6,6'-H biphenolate), 7.29 (d, 8 Hz, 4H, Tol 2,6-H), 7.38 (d, 2.5 Hz, 2H, 4,4'-H biphenolate), 7.42 (dd, 7.5, 1.5 Hz, 2H, 6-H biphenyl), 7.48 (td, 7.5, 1.5 Hz, 2H, 5-H biphenyl). ¹³C{¹H} NMR (CD₂Cl₂): δ 21.92 (tolyl CH₃), 31.09

(C(CH₃)₃), 32.03 (C(CH₃)₃), 34.93 (C(CH₃)₃), 35.77 (C(CH₃)₃), 46.37 (CH₂), 102.55 (COCHCO), 123.36, 127.57, 128.47, 128.79, 128.91, 129.28, 130.03, 130.09, 132.42, 133.59, 134.98, 137.22, 140.83, 143.29, 143.73, 161.58, 180.95 (CO), 191.17 (CO). IR (cm⁻¹): 2953 (m), 2903 (w), 2868 (w), 1592 (m), 1546 (m), 1519 (s), 1498 (s), 1422 (w), 1361 (m), 1323 (m), 1298 (w), 1283 (w), 1263 (w), 1242 (w), 1184 (m), 1097 (m), 985 (m), 861 (m), 775 (m), 751 (m). FABMS: *m/z* 957 (M+H)⁺. Anal. Calcd for C₆₂H₆₈O₆Ti: C, 77.81; H, 7.16. Found: C, 78.03; H, 7.69.

(Hox)Ti(O₂C₁₂H₄'Bu₄). This compound was prepared by the procedure described for (Bob)Ti(O₂C₁₂H₄'Bu₄) using (Hox)Ti(O^{*i*}Pr)₂ (0.0980 g, 0.199 mmol) and 3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (0.0823 g, 0.200 mmol), except that the eluent used for chromatography was 2:1 hexanes/ethyl acetate. Yield: 0.0418 g (27%). ¹H NMR (CD₂Cl₂): δ 1.32 (s, 18H, C(CH₃)₃), 1.37 (s, 18H, C(CH₃)₃), 2.72 (s, 6H, NCH₃), 3.42 (d, 16 Hz, 2H, CHH'), 4.10 (d, 16 Hz, 2H, CHH'), 6.99 (d, 2.5 Hz, 2H, 4-H biphenolate), 7.29 (m, 2H, Ar-H biphenyl), 7.29 (d, 2.5 Hz, 2H, 6-H biphenolate), 7.43 (m, 6H, Ar-H biphenyl). ¹³C{¹H} NMR (CD₂Cl₂): δ 31.19 (C(CH₃)₃), 31.92 (C(CH₃)₃), 34.79 (C(CH₃)₃), 34.83 (NCH₃), 35.73 (C(CH₃)₃), 38.27 (CH₂), 123.69, 128.17, 128.19, 128.57, 129.34, 130.02, 133.88, 134.41, 135.72, 139.69, 142.62, 159.49, 164.82 (CO). IR (cm⁻¹): 2953 (s), 2906 (m), 2868 (w), 1590 (s, ν_{CO}), 1479 (m), 1427 (s), 1402 (m), 1390 (w), 1361 (w), 1269 (s), 1242 (s), 1136 (w), 1097 (w), 995 (w), 914 (w), 880 (w), 852 (m), 822 (w), 796 (w), 765 (w), 753 (s), 744 (s), 668 (w). FABMS: *m/z* 783 (M+H)⁺. Anal. Calcd for C₄₆H₅₈N₂O₆Ti: C, 70.58; H, 7.47; N, 3.58. Found: C, 71.17; H, 7.73; N, 3.23.

(Hob)Ti(O₂C₁₂H₄'Bu₄). This compound was prepared by the procedure described for (Bob)Ti(O₂C₁₂H₄'Bu₄) using (Hob)Ti(O^{*i*}Pr)₂ (0.0887 g, 0.153 mmol) and 3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (0.0630 g, 0.153 mmol). In this case, chromatography was not necessary, instead the deep red residue was purified by suspending in 4 mL of hexanes, filtering,

and washing with 2×1 mL of hexanes. After drying *in vacuo* 1 h, 0.0949 g of the complex was isolated (71%). ^1H NMR (CD_2Cl_2): δ 1.20 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.37 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.43 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.34 (s, 3H, tolyl CH_3), 2.62 (s, 3H, NCH_3), 3.31 (d, 15 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 3.42 (d, 15.5 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 4.08 (d, 15 Hz, 1H, $\text{CH}_c\text{H}_d\text{COCHCOTol}$), 4.11 (d, 15.5 Hz, 1H, $\text{CH}_a\text{H}_b\text{CON}(\text{CH}_3)\text{O}$), 5.70 (s, 1H, COCHCO), 7.03 (d, 2.5 Hz, 1H, 4-H biphenolate), 7.04 (d, 8 Hz, 2H, Tol 3,5-H), 7.06 (d, 2.5 Hz, 1H, 4'-H biphenolate), 7.15 (d, 8 Hz, 2H, Tol 2,6-H), 7.24 (dd, 7.5, 2 Hz, 1H, 3- or 3'-H biphenyl), 7.29 (td, 7.5, 2 Hz, 1H, 4- or 4'-H biphenyl), 7.30 (d, 2.5 Hz, 1H, 6-H biphenolate), 7.31 (dd, 7.5, 2 Hz, 1H, 3- or 3'-H biphenyl), 7.37 (dd, 7.5, 2.0 Hz, 1H, 6- or 6'-H biphenyl), 7.40 (d, 2.5 Hz, 1H, 6'-H biphenolate), 7.40 (td, 7.5, 2 Hz, 1H, 4- or 4'-H biphenyl), 7.41 (dd, 7.5, 2 Hz, 1H, 6- or 6'-H biphenyl), 7.42 (td, 7.5, 2 Hz, 1H, 5- or 5'-H biphenyl), 7.48 (td, 7.5, 2 Hz, 1H, 5- or 5'-H biphenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 21.89 (tolyl CH_3), 30.99 ($\text{C}(\text{CH}_3)_3$), 31.18 ($\text{C}(\text{CH}_3)_3$), 31.95 ($\text{C}(\text{CH}_3)_3$), 32.05 ($\text{C}(\text{CH}_3)_3$), 34.84 ($\text{C}(\text{CH}_3)_3$), 34.91 ($\text{C}(\text{CH}_3)_3$), 34.94 (NCH_3), 35.65 ($\text{C}(\text{CH}_3)_3$), 35.84 ($\text{C}(\text{CH}_3)_3$), 38.56 (CH_2 hydroxamate), 46.24 (CH_2 diketonate), 101.53 (COCHCO), 123.33, 123.62, 127.58, 128.02, 128.04, 128.33, 128.38, 128.58, 128.64, 128.70, 129.27, 129.91, 130.33, 130.56, 132.62, 133.44, 134.01, 134.44, 134.88, 135.61, 137.51, 139.89, 140.52, 142.70, 143.48, 143.60, 160.32, 160.84, 163.88 (CO hydroxamate), 180.29 (CO diketonate), 192.90 (CO diketonate). IR (cm^{-1}): 2953 (s), 2906 (m), 2868 (m), 1587 (s, ν_{CO}), 1561 (m), 1520 (s), 1498 (s), 1476 (m), 1422 (m), 1402 (w), 1362 (m), 1329 (w), 1266 (m), 1243 (m), 1185 (w), 1134 (w), 1128 (w), 1098 (m), 879 (w), 860 (m), 765 (w), 752 (m), 742 (m). FABMS: m/z 870 ($\text{M}+\text{H}$)⁺. Anal. Calcd for $\text{C}_{54}\text{H}_{63}\text{NO}_6\text{Ti}$: C, 74.55; H, 7.30; N, 1.61. Found: C, 75.04; H, 8.05; N, 1.40.

II. X-ray Crystallography

X-ray crystallography of (Bob)Ti(O₂C₁₂H₄[CH₃])₄ • 0.5 C₆H₁₄. Crystals were grown from a saturated solution of the complex in hexanes at room temperature. An arbitrary sphere of data was collected at beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory, on a red plate-like crystal, having approximate dimensions of 0.04 × 0.03 × 0.01 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.3° at 150(2) K. Data were reduced, correcting for absorption and polarization, and the space group was assigned using standard methods.⁶ The structure was solved by direct methods, and nonhydrogen atoms not apparent in the initial solution were found on subsequent difference Fourier maps. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were included in calculated positions, with thermal parameters for the hydrogens tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others). Calculations used SHELXTL (Bruker AXS),^{S7} with scattering factors and anomalous dispersion terms taken from the literature.^{S8} Further details about the structure are in Table S1.

X-ray crystallography of (Hox)Ti(O₂C₁₂H₄[CH₃])₄ • CD₂Cl₂, (Hob)Ti(O₂C₁₂H₄[CH₃])₄ • CDCl₃ and (Hob)Ti(O₂C₁₂H₄[NO₂])₄ • 2 CHCl₃. (Hox)Ti(O₂C₁₂H₄[CH₃])₄ • CD₂Cl₂ and (Hob)Ti(O₂C₁₂H₄[CH₃])₄ • CDCl₃ were grown from concentrated solutions of CD₂Cl₂ and CDCl₃ respectively at room temperature. Crystals of (Hob)Ti(O₂C₁₂H₄[NO₂])₄ • 2 CHCl₃ were grown by layering of hexanes over a concentrated solution of the complex in CHCl₃. The crystals were placed in inert oil and transferred to a nylon loop in the cold N₂ stream of a Bruker Apex CCD diffractometer ($T = 100$ K). Data reduction, structure solution and refinement were performed as

described above, except for the treatment of hydrogen atoms. In these structures, the hydrogen atoms were found on difference Fourier maps and refined isotropically, except for the hydrogens on methyl groups C58 and C68 in $(\text{Hob})\text{Ti}(\text{O}_2\text{C}_{12}\text{H}_4[\text{CH}_3])_4 \cdot \text{CDCl}_3$, which were placed in calculated positions. One of the chloroforms of solvation in $(\text{Hob})\text{Ti}(\text{O}_2\text{C}_{12}\text{H}_4[\text{NO}_2])_4 \cdot 2 \text{CDCl}_3$ was disordered over two orientations (the major refined to 88.2(2)% occupancy). Details about the structures are in Table S2.

Table S1. Crystal data for (Bob)Ti(O₂C₁₂H₄[CH₃])₄ • 0.5 C₆H₁₄.

(Bob)Ti(O ₂ C ₁₂ H ₄ [CH ₃]) ₄ • 0.5 C ₆ H ₁₄	
Molecular formula	C ₅₃ H ₅₁ O ₆ Ti
Formula weight	831.84
<i>T</i> / K	150(2)
λ / Å	0.77490
Crystal system	Triclinic
Space group	$P\bar{1}$
Total data collected	11691
No. of indep reflns.	3568
<i>R</i> _{int}	0.0619
Obsd. refls. [<i>I</i> > 2σ(<i>I</i>)]	2563
<i>a</i> / Å	9.5360(15)
<i>b</i> / Å	10.7745(17)
<i>c</i> / Å	21.214(3)
α / °	87.903(2)
β / °	87.712(3)
γ / °	88.606(2)
<i>V</i> / Å ³	2175.9(6)
<i>Z</i>	2
Cryst size / mm	0.04 × 0.03 × 0.01
No. refined params.	547
R indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0400, <i>wR</i> 2 = 0.0927
R indices (all data) ^a	<i>R</i> 1 = 0.0677, <i>wR</i> 2 = 0.1056
Goodness of fit	1.003

^a $R1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; $wR2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2)^{1/2}$.

Table S2. Crystal data for (Hox)Ti(O₂C₁₂H₄[CH₃])₄ • CD₂Cl₂, (Hob)Ti(O₂C₁₂H₄[CH₃])₄ • CDCl₃ and (Hob)Ti(O₂C₁₂H₄[NO₂])₄ • 2 CDCl₃.

	(Hox)Ti(O ₂ C ₁₂ H ₄ [CH ₃]) ₄ • CD ₂ Cl ₂	(Hob)Ti(O ₂ C ₁₂ H ₄ [CH ₃]) ₄ • CDCl ₃	(Hob)Ti(O ₂ C ₁₂ H ₄ [NO ₂]) ₄ • 2 CHCl ₃
Molecular formula	C ₃₅ H ₃₄ D ₂ Cl ₂ N ₂ O ₆ Ti	C ₄₃ H ₄₀ Cl ₃ NO ₆ Ti	C ₄₀ H ₂₉ Cl ₆ N ₅ O ₁₄ Ti
Formula weight	701.46	822.01	1064.28
<i>T</i> / K	100(2)	99(2)	100(2)
λ / nm	0.71073 (Mo K α)	0.71073 (Mo K α)	0.71073 (Mo K α)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Total data collected	47756	28893	33459
No. of indep reflns.	6802	7854	9014
<i>R</i> _{int}	0.0411	0.0326	0.0516
Obsd. refls. [<i>I</i> > 2 σ (<i>I</i>)]	5763	6583	6501
<i>a</i> / Å	12.3148(13)	12.0648(5)	11.2931(4)
<i>b</i> / Å	13.2234(14)	12.6467(5)	13.3440(5)
<i>c</i> / Å	20.372(2)	14.4497(14)	15.1141(6)
α / °	90	109.3684(14)	96.792(2)
β / °	94.7950(16)	96.4954(15)	102.423(2)
γ / °	90	106.9980(17)	93.434(3)
<i>V</i> / Å ³	3305.9(6)	1934.4(2)	2200.11(14)
<i>Z</i>	4	2	2
Cryst size / mm	0.29 × 0.10 × 0.08	0.26 × 0.20 × 0.16	0.145 × 0.08 × 0.07
No. refined params.	559	625	718
R indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.0307, <i>wR</i> 2 = 0.0792	<i>R</i> 1 = 0.0374, <i>wR</i> 2 = 0.0932	<i>R</i> 1 = 0.0449, <i>wR</i> 2 = 0.1020
R indices (all data) ^a	<i>R</i> 1 = 0.0392, <i>wR</i> 2 = 0.0846	<i>R</i> 1 = 0.0473, <i>wR</i> 2 = 0.0993	<i>R</i> 1 = 0.0746, <i>wR</i> 2 = 0.1150
Goodness of fit	1.030	1.037	1.024

^a *R*1 = $\sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; *wR*2 = $(\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2)^{1/2}$.

III. DFT Calculations

A. General considerations

All calculations employed the hybrid B3LYP method, with a 6-31G* basis set for all atoms, using the Gaussian03 suite of programs.^{S9} Optimized geometries were confirmed to be minima by frequency analysis. While the symmetries of the molecules were not constrained in the calculation, the final geometries of (acac)₂TiCl₂ and (CH₃CON[CH₃]O)₂TiCl₂ were extremely close to C₂ symmetry. The Kohn-Sham orbital representations were created in GaussView (v. 3.09) using a contour value of 0.03.

B. (acac)₂TiCl₂ (*cis*)

Energy of optimized structure: -2460.50833 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	22	0.000127	-0.730878	-0.000443
2	8	0.669488	0.819216	-1.172252
3	8	-0.671434	0.814463	1.176011
4	8	1.706349	-0.477309	0.892879
5	8	-1.706277	-0.476791	-0.893407
6	6	2.738524	0.277574	0.723560
7	6	2.822597	1.234613	-0.283007
8	1	3.725513	1.825641	-0.370195
9	6	1.772888	1.453372	-1.198234
10	6	1.918391	2.478422	-2.295281
11	1	2.854676	3.036598	-2.222574
12	1	1.877948	1.969726	-3.265536
13	1	1.073634	3.174792	-2.261072
14	6	3.864586	0.045964	1.693656
15	1	4.706677	0.719125	1.517524
16	1	3.496478	0.180468	2.716987
17	1	4.205703	-0.992236	1.609923
18	6	-1.774712	1.448857	1.202278
19	6	-2.823218	1.232928	0.285039
20	6	-2.738339	0.278106	-0.723587
21	6	-3.863508	0.048908	-1.695293
22	1	-4.705318	0.722372	-1.518969
23	1	-3.494169	0.184829	-2.717990
24	1	-4.205474	-0.989183	-1.613651
25	6	-1.921247	2.471024	2.301868
26	1	-1.078665	3.170062	2.267469

27	1	-1.877287	1.960422	3.270938
28	1	-2.859266	3.026644	2.232073
29	1	-3.726102	1.823943	0.372642
30	17	-0.764756	-2.208688	1.541208
31	17	0.767231	-2.202437	-1.547070

C. (CH₃CON[CH₃]O)₂TiCl₂ (*cis-α*, equatorial carbonyls)

Energy of minimized structure: -2416.29569 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	22	-0.000017	0.729457	0.000015
2	8	-0.890822	-0.871199	1.053742
3	8	-1.651852	0.389301	-0.943331
4	8	0.891058	-0.870851	-1.054024
5	8	1.651855	0.389367	0.943319
6	17	0.635784	2.181437	-1.619240
7	17	-0.636089	2.180999	1.619563
8	7	-2.453396	-0.614974	-0.489183
9	7	2.453516	-0.614747	0.489035
10	6	-2.787121	-2.365632	1.230721
11	1	-2.202315	-2.743638	2.069931
12	1	-3.752393	-2.009920	1.606879
13	1	-2.973251	-3.184833	0.528183
14	6	-2.007029	-1.249479	0.587892
15	6	-3.673929	-0.799639	-1.247201
16	1	-4.257118	0.125606	-1.220825
17	1	-4.255991	-1.614925	-0.815802
18	1	-3.419733	-1.033094	-2.285319
19	6	2.787427	-2.365220	-1.231005
20	1	2.203833	-2.741484	-2.071834
21	1	2.971177	-3.185559	-0.529138
22	1	3.753868	-2.010182	-1.604745
23	6	2.007263	-1.249120	-0.588165
24	6	3.673801	-0.799777	1.247358
25	1	3.419282	-1.033666	2.285297
26	1	4.257040	0.125454	1.221554
27	1	4.255947	-1.614918	0.815793

D. (CH₃CON[CH₃]O)(acac)TiCl₂ (*cis*, equatorial carbonyl)

Energy of optimized structure: -2438.40123 a.u.

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	22	-0.050194	-0.702846	0.225039
2	8	0.750721	1.031989	0.986033
3	8	1.588985	-0.675834	-0.840709
4	8	-0.841834	0.631422	-1.207268
5	8	-1.750343	-0.182939	0.948302
6	17	-0.812001	-2.470102	-1.004538
7	17	0.570463	-1.800265	2.093463
8	7	-2.542501	0.640489	0.206050
9	6	2.045180	2.923449	1.553877
10	1	1.167967	3.576987	1.497218
11	1	2.932387	3.476207	1.236158
12	1	2.160937	2.630799	2.603940
13	6	1.809341	1.686800	0.721862
14	6	2.737535	1.303610	-0.266256
15	1	3.609849	1.921682	-0.437952
16	6	2.585644	0.127376	-0.994697
17	6	-2.758495	1.931409	-1.899714
18	1	-2.042671	2.324752	-2.622744
19	1	-3.517685	1.356583	-2.442552
20	1	-3.252513	2.765731	-1.393798
21	6	-2.010442	1.043288	-0.942985
22	6	-3.850872	0.886717	0.779006
23	1	-3.729918	1.346089	1.764313
24	1	-4.420405	1.549817	0.127210
25	1	-4.378784	-0.065089	0.888601
26	6	3.602366	-0.307693	-2.015388
27	1	3.109852	-0.432875	-2.986252
28	1	4.424233	0.405587	-2.112182
29	1	4.002897	-1.287673	-1.731976

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