Optically active bis(β-diketonate) complexes of titanium†

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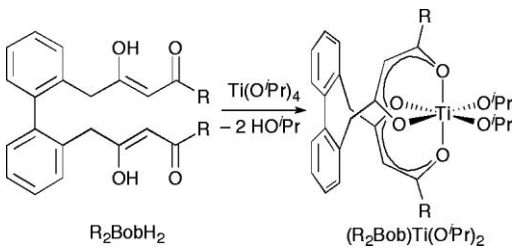
The 2,2′-bis(methylene)biphenyl bridged bis(diketonate) (Tol_2Bob)Ti^{IV} fragment is resolved by reaction of the isopropoxide complex with (*R*)-1,1′-bi-2-naphthol, which selectively forms (*S*,Δ)-(Tol_2Bob)Ti(*R*-BINOL). The binaphtholate ligand can be cleaved from titanium by careful treatment with trifluoromethanesulfonic acid to give (*S*,Δ)-(Tol_2Bob)$Ti(OTf)_2$, which has a half-life toward racemization of at least 34 h at 51 °C. Racemization of the (Tol_2Bob)Ti^{IV} fragment is strongly accelerated under protic conditions, probably due to protonolysis of one of the diketonate ligands. Analogous optically active titanium bis(diketonates) can also be prepared by using an optically active 2,2′-bis(methylene)-1,1′-binaphthyl bridged bis(diketonate) ligand, Tol_2Bobbinap, prepared from (*R*)-BINOLH2. Complexation of (*R*)-Tol_2BobbinapH_2 with $Ti(OiPr)_4$ gives only a single diastereomer with the Λ configuration at titanium. The bis(diketonate)titanium(IV) fragment gives rise to characteristic signals in circular dichroism spectra which can be used to identify the configuration at the metal centre.

Introduction

Optically active transition metal complexes are of central importance in the development of enantioselective metal-catalyzed reactions. In most cases, the dissymmetric environment is provided by an optically active organic ligand. Optically active metal complexes containing achiral ligands—in other words, complexes where the metal itself is the only chiral center—have been known for over a century and played a key role in the elucidation of the octahedral geometry of six-coordinate complexes.[1] Such complexes have, however, attracted relatively little attention for their potential use in asymmetric catalysis.[2]

One limitation of chiral-at-metal complexes in these applications is that while it is relatively easy to resolve kinetically inert complexes, they tend to be unreactive in catalytic reactions, while labile complexes that are potentially reactive are difficult to resolve. A case in point involves octahedral *cis*-bis(diketonato)titanium(IV) complexes. The bis(diketonate)titanium(IV) fragment has been shown to be remarkably selective in its binding to 1,1′-bi-2-naphtholate (BINOL), and its selectivity has been attributed to its dissymmetric *electronic* structure rather than to any significant nonbonding interactions with the BINOL moiety.[3] It would be intriguing to apply this electronic stereochemical control element in a catalytic reaction. Unfortunately, the well-known proclivity of bis(diketonate)titanium(IV) compounds to undergo trigonal twists, resulting in racemization of the metal center on the NMR timescale,[4] would seem to preclude any application of this metal-based chirality in asymmetric synthesis.

More recently, we reported that bis(diketonates) with a 2,2′-bis(methylene)biphenyl bridge between the diketonate ligands ("R_2Bob" ligands) readily form *cis*-α chelates with titanium(IV) (*e.g.*, eqn (1)).[5] Compared to titanium complexes of simple unlinked diketonates, these complexes show greatly enhanced optical stability (they are not fluxional by NMR spectroscopy), and there is a strong linkage between the configuration of the biphenyl backbone and the configuration at titanium (only the (*S*,Δ)/(*R*,Λ) diastereomer is observed). Analogous complexes with hydroxamates replacing one or both of the diketonates appear to share these stereochemical features.[6]



(1)

Here we describe the resolution of the (Tol_2Bob)Ti^{IV} fragment by its complexation with optically active BINOL. Cleavage of the binaphtholate results in production of a reactive titanium fragment with moderate optical stability, although protic conditions result in rather facile racemization. The successful implementation of an alternative strategy to form an optically active bis(diketonate)titanium fragment, by using an optically active 2,2′-bis(methylene)binaphthyl (rather than -biphenyl) linker, is also described.

Experimental

General procedures

Unless otherwise noted, all procedures were carried out under inert atmosphere using standard vacuum line or drybox techniques. Methylene chloride and chloroform were dried over 4 Å molecular sieves, then transferred over calcium hydride. Diethyl ether was dried over sodium/benzophenone, and hydrocarbon solvents over

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sodium. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried in the same way as their protio analogues. Dry solvents were vacuum transferred from their respective drying agents either directly into reaction flasks, or were stored in the drybox before use. Titanium tetraisopropoxide (Aldrich), (*R*)- or (*S*)-1,1′-bi-2-naphthol (BINOLH_2, TCI America) and (*R*,*R*)- and (*S*,*S*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (TaddolH_2, Strem or Aldrich) were commercial products and were used without further purification.

NMR spectra were measured on a Varian VXR-300 or VXR-500 FT-NMR spectrometer and are reported in ppm downfield of TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F). Infrared spectra were recorded as nujol mulls on KBr plates on a Perkin Elmer Paragon 1000 FT-IR spectrometer. UV-visible spectra were collected on a Beckman DU-7500 diode-array spectrophotometer with samples in 1 cm quartz cuvettes whose temperature was maintained by circulating a water–ethylene glycol mixture through the cell block. Mass spectra were obtained on a JEOL JMS-AX 505HA mass spectrometer using the FAB ionization mode and 3-nitrobenzylalcohol as a matrix. In all cases, observed intensities were in satisfactory agreement with calculated isotopic distributions. Circular dichroism spectra were obtained as CH_2Cl_2 solutions (~5×10^{-5} M) on an Aviv 62D2 spectropolarimeter. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

Preparation of (Tol$_2$Bob)Ti complexes

(*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL). In the drybox, 1.0294 g (Tol$_2$Bob)Ti(O^{i}Pr)$_2$[5] (1.5441 mmol) was placed in a scintillation vial with 0.2230 g (*R*)-1,1′-binaphthyl-2,2′-diol (0.7788 mmol, 0.50 equiv). The contents of the vial were dissolved in dry benzene, which immediately turned a deep red color. The vial was allowed to stand for one week, during which time a mixture of desired product and starting material precipitated. The supernatant was pipetted out of the vial and transferred to a small round-bottom flask. The solid product was washed with 7 mL dry benzene to remove the diisopropoxide complex, and the wash added to the supernatant. The contents of the flask were then stripped down on a rotary evaporator (in the air) and were returned to the drybox to be redissolved in a minimal amount of dry benzene. Crystals were harvested from this solution twice more in the manner described above for a final yield of 0.4504 grams of air-stable (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) (0.5408 mmol, 70% yield based on BINOL). If crystallization does not take place, the compound can be purified by chromatography on silica gel in the air, eluting with $CHCl_3$. The (*R*,Λ,*S*) isomer is prepared analogously using (*S*)-BINOLH_2. ^{1}H NMR ($CDCl_3$): δ 2.42 (s, 6H, *CH*$_3$), 3.34 (d, 14 Hz, 2H, C*H*H′), 4.04 (d, 14 Hz, 2H, CH*H*′), 5.54 (s, 2H, COC*H*CO), 7.14 (d, 9 Hz, 4H, Tol 3,5-H), 7.21 (m, 10H, ArH), 7.40 (m, 4H, ArH), 7.42 (d, 9 Hz, 4H, Tol 2,6-H), 7.49 (td, 7, 1.5 Hz, 2H, biphenyl 4- or 5-H), 7.90 (d, 8 Hz, 2H, BINOL 5-H), 7.94 (d, 9 Hz, 2H, BINOL 3-H). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.83 (*C*H$_3$), 46.14 (*C*H$_2$), 103.90 (CO*C*HCO), 117.61, 121.25, 123.71, 126.30, 127.43, 128.45, 128.61, 129.08, 129.37, 129.46, 130.13, 131.08, 132.96, 134.11, 135.08, 137.05, 140.99, 143.49, 164.41 (BINOL C2), 181.78 (CH$_2$*C*O), 191.74 (Tol*C*O); one carbon not found. IR (KBr, cm^{-1}): 3054 (m), 3030 (m), 3013 (m), 1606 (m), 1579 (m), 1544 (w), 1520 (w), 1499 (w), 1472 (m), 1460 (m), 1438 (m), 1424 (m), 1358 (w), 1321 (w), 1301 (m), 1285 (m), 1269 (m), 1240 (w), 1219 (m), 1184 (m), 1158 (m), 1120 (s), 1100 (s), 1071 (s), 1051 (s), 1015 (s), 984 (m), 953 (m), 887 (s), 867 (s), 856 (s), 845 (s), 835 (s), 818 (w), 794 (m), 769 (s), 750 (m), 738 (m), 724 (s), 714 (s), 690 (s), 679 (m), 669 (s), 639 (s), 622 (s), 603 (m), 590 (s), 568 (s), 540 (s), 536 (m), 524 (m), 510 (m), 494 (s), 474 (s). FAB-MS: *m*/*z* = 833 (M + H$^+$). UV-Vis (CH_2Cl_2): λ_{max} 388 nm (ε = 1.7×10^4 M^{-1} cm^{-1}), 292 (3.4×10^4). CD (CH_2Cl_2): 485 nm (Δε = −5 M^{-1} cm^{-1}), 430 (−7), 370 (−38), 321 (+31), 288 (+28), 261 (−86). Anal. Calcd for $C_{54}H_{40}O_6Ti$: C, 77.88; H, 4.84. Found C, 78.05; H, 5.14.

(*S*,Δ)-(Tol$_2$Bob)Ti(OTf)$_2$. In the drybox, (*S*,Δ,*R*)-(Tol$_2$Bob)-Ti(BINOL) (0.2017 g, 0.24 mmol), a magnetic stirrer bar and 8 mL CH_2Cl_2 were added into a scintillation vial. The solution was stirred until all the solid dissolved, then transferred into a 250 mL Erlenmeyer flask. Into another scintillation vial, triflic acid (0.0727 g, 0.48 mmol) was weighed and dissolved in 3 mL CH_2Cl_2. The triflic acid solution was added to the solution of the binaphtholate complex with rapid stirring. Immediately upon the completion of addition, 70 mL of hexane was added. The dark brown precipitate was filtered, washed with 2 × 3 mL of hexanes and dried *in vacuo* for 1 h. Yield: 0.1533 g (75%; the product is contaminated with a small amount of the starting binaphtholate). NMR data were identical to those previously reported for the racemic material.[5]

(*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol). In the drybox, (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) (0.3063 g, 0.37 mmol), (*R*,*R*)-TaddolH_2 (0.1907 g, 0.41 mmol), 12 mL of chloroform and a magnetic stirrer bar were added to a 20 mL vial. The vial was capped tightly and taken out of the drybox. The mixture was heated for 5 d in a 50 °C oil bath. After evaporation of the solvent, the residue was redissolved in 4 mL benzene in the air, and then 12 mL hexane was added. After standing at room temperature overnight, the reddish brown precipitate was filtered and washed with 2 × 1 mL hexanes. The precipitate was then redissolved in 4 mL dichloromethane and layered with 8 mL of hexanes. After standing at room temperature for a few hours, deep red crystals of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) precipitated. The mixture was allowed to stand until the first yellow crystals of the product appeared (~5 h), at which point the solution was decanted away from the red crystals, which were discarded. After standing at room temperature overnight, the product precipitated out as yellow crystals which were isolated by decantation and washing with 2 × 1 mL hexanes. The decanted solution and washes were collected and allowed to stand at room temperature until another crop of product formed, and the process repeated to give a total of four crops of (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol), for a total combined yield of 0.1083 g (29%). ^{1}H NMR ($CDCl_3$): δ 0.66 (s, 6H, C(C*H*$_3$)$_2$), 2.41 (s, 6H, tolyl C*H*$_3$), 3.15 (d, 14 Hz, 2H, C*H*H′), 3.93 (d, 14 Hz, 2H, CH*H*′), 5.25 (s, 2H, COC*H*CO), 5.30 (s, 2H, Taddol OC*H*), 6.99 (m, 16H, ArH), 7.30 (m, 12H, ArH), 7.33 (dd, 7, 1.5 Hz, 4H, Taddol *o*-C$_6$H$_5$), 7.80 (dd, 7, 1.5 Hz, 4H, Taddol *o*-C$_6$H$_5$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.84 (C(*C*H$_3$)$_2$), 27.52 (tolyl *C*H$_3$), 46.33 (*C*H$_2$), 82.46 (Taddol O*C*H), 95.32 (Taddol Ph$_2$*C*OTi), 101.05 (CO*C*HCO), 110.33 (Taddol O*C*(CH$_3$)$_2$O), 126.43, 126.77, 126.83, 126.87, 127.80, 127.84, 128.05, 128.26, 128.99, 129.35, 129.46, 133.24, 133.41, 137.01, 140.47, 142.02, 144.17, 148.12, 179.92 (CH$_2$*C*O), 190.63 (Tol*C*O). IR (evapd film, cm^{-1}): 3058 (w), 3022 (w), 2989 (w), 2921 (w), 1594 (m), 1582 (m), 1560 (m),

1547 (m), 1519 (s), 1496 (s), 1447 (w), 1425 (w), 1412 (w), 1368 (s), 1323 (m), 1299 (w), 1242 (w), 1215 (w), 1184 (m), 1163 (w), 1120 (m), 1097 (m), 1074 (m), 1020 (m), 983 (m), 889 (m), 824 (w), 796 (m), 776 (m), 728 (m), 697 (m), 640 (m). UV-Vis (CH_2Cl_2): λ_{max} 380 nm ($\varepsilon = 2.3 \times 10^4$ M^{-1} cm^{-1}), 285 (3.6×10^4). CD (CH_2Cl_2): 367 nm ($\Delta\varepsilon$ = −39 M^{-1} cm^{-1}), 319 sh (+21), 294 (+34). FABMS: *m/z* 1012 (M^+). Anal. Calcd for $C_{65}H_{56}O_8Ti$: C, 77.07; H, 5.57. Found: C, 77.23; H, 5.34.

(*S*,Δ,*S*,*S*)-(Tol$_2$Bob)Ti(Taddol). This compound was prepared using (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) (0.2684 g, 0.32 mmol) and (*S*,*S*)-TaddolH$_2$ (0.1667 g, 0.36 mmol) by the same procedure described for (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol) up through the point at which the crude reaction mixture was stripped down on a rotary evaporator. At this point, the residue was dissolved in 4 mL benzene and a reddish brown powder was precipitated by addition of 12 mL hexanes. After filtration and washing with 2 × 1 mL of hexanes, the precipitate was redissolved in 4 mL of dichloromethane and layered with 8 mL of hexanes. After standing at room temperature for a few hours, deep red crystals of unreacted (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) formed. After standing at room temperature overnight, the supernatant was pipetted away from the red crystals and stripped down on a rotary evaporator. The orange residue was dissolved in 2 mL CH_2Cl_2 and precipitated with 4 mL hexanes. The yellow precipitate was collected by filtration and washed with 2 × 1 mL hexanes. The filtrate was collected, evaporated to dryness, and a second crystallization from CH_2Cl_2/hexanes (1 mL : 2 mL) yielded a second crop of product, for a combined yield of 0.1024 g (*S*,Δ,*S*,*S*)-(Tol$_2$Bob)Ti(Taddol) (31%). ^{1}H NMR ($CDCl_3$): δ 0.70 (s, 6H, C(C*H*$_3$)$_2$), 2.43 (s, 6H, tolyl C*H*$_3$), 3.22 (d, 14 Hz, 2H, C*H*H′), 3.93 (d, 14 Hz, 2H, CH*H*′), 5.17 (s, 2H, COC*H*CO), 5.19 (s, 2H, Taddol OC*H*), 6.91 (t, 7 Hz, 2H, Taddol *p*-C$_6$H$_5$), 7.01 (t, 7 Hz, 4H, Taddol *m*-C$_6$H$_5$), 7.10 (t, 8 Hz, 2H, biphenyl 4- or 5-H), 7.16 (m, 12H, ArH), 7.30 (d, 8 Hz, 4H, Tol 2,6-H), 7.33 (d, 8 Hz, 2H, biphenyl 3- or 6-H), 7.40 (t, 7 Hz, 2H, biphenyl 4- or 5-H), 7.56 (d, 8 Hz, 4H, Taddol *o*-C$_6$H$_5$), 7.71 (m, 4H, Taddol *o*-C$_6$H$_5$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.82 (Taddol C(*C*H$_3$)$_2$), 27.46 (tolyl *C*H$_3$), 46.12 (*C*H$_2$), 83.36 (Taddol O*C*H), 95.98 (Taddol Ph$_2$*C*OTi), 101.64 (CO*C*HCO), 110.45 (Taddol O*C*(CH$_3$)$_2$O), 126.48, 126.67, 126.96, 127.55, 127.76, 128.05, 128.81, 129.48, 129.86, 133.70, 134.26, 136.88, 140.53, 141.90, 143.62, 147.98, 180.98 (CH$_2$*C*O), 191.17 (Tol*C*O); two aromatic carbons overlapped with other signals. IR (evapd film, cm^{-1}): 3056 (w), 3022 (w), 2994 (w), 2924 (w), 1594 (s), 1561 (m), 1519 (s), 1497 (s), 1447 (m), 1423 (m), 1413 (m), 1367 (s), 1327 (m), 1302 (m), 1244 (w), 1213 (w), 1185 (m), 1163 (m), 1119 (m), 1097 (m), 1073 (s), 1020 (m), 983 (m), 887 (m), 825 (w), 779 (m), 748 (m), 719 (m), 697 (m), 680 (m), 640 (m). FABMS: *m/z* 1013 (M+H$^+$). UV-Vis (CH_2Cl_2): λ_{max} = 290 nm, $\varepsilon = 4.4 \times 10^4$ M^{-1} cm^{-1}; λ_{max} = 385 nm, $\varepsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}. CD (CH_2Cl_2): 372 nm ($\Delta\varepsilon$ = −23 M^{-1} cm^{-1}), 307 (+26). Anal. Calcd for $C_{65}H_{56}O_8Ti$: C, 77.07; H, 5.57. Found: C, 77.10; H, 5.64.

Preparation of BobbinapH$_2$

(*R*)-1,1′-Binaphthyl-2,2′-diacetic acid, (*R*)-(C$_{10}$H$_6$-2-CH$_2$CO$_2$H)$_2$. (*R*)-2,2′-Dimethyl-1,1′-binaphthyl[7] (9.0563 g, 32.10 mmol) was lithiated using *n*-BuLi/TMEDA according to the published procedures,[8] with the crystalline organolithium isolated by decantation and washing with hexane, and a second crop isolated after the washes were allowed to stand at −35 °C overnight. (The washes from the lithiation procedure after the crystallization of the second crop of lithio compound were quenched with aqueous NH_4Cl to recover 1.3908 g dimethylbinaphthyl [15%].) Each crop of the crystalline lithium compound was carboxylated by the following procedure: the material was placed in a three-neck round bottom flask with a Teflon needle valve and sealed with rubber septa, which was taken out of the drybox and affixed to a vacuum line. Ether (40 mL) was added by vacuum transfer. After that, under nitrogen flow one of the rubber septa was replaced with a one-arm tee vented to a bubbler. At −78 °C, with the needle valve closed, the second rubber septum was taken out, about 2 g of dry ice were added, and the septum replaced. The dark red suspension turned clear yellow, and a light yellow precipitate formed. After stirring at −78 °C for 10 min, the precipitate was filtered through a glass frit in the open air, washed with 2 × 10 mL ice-cold ether and transferred into a 250 mL round bottom flask. The solid was digested by stirring with methylene chloride (80 mL) and 6 M HCl (40 mL) until it had completely dissolved. The mixture was poured into a 500 mL separatory funnel, and the top water layer was discarded. A clear light yellow organic layer was collected, dried over $MgSO_4$, filtered and stripped down on a rotary evaporator. The yellow residue was stirred in 20 mL $CHCl_3$ and the white precipitate isolated by filtration and washing with 2 × 5 mL chloroform. A second crop of the product was obtained by stripping down the filtrate, resuspending in chloroform, and filtering. The combined yield of (*R*)-1,1′-binaphthyl-2,2′-diacetic acid was 4.5890 g (39%; 46% based on recovered starting material). ^{1}H NMR (acetone-d_6): δ 3.40 (AB quartet, $\Delta\delta_{AB}$ = 0.03 ppm, J_{AB} = 16.5 Hz, 4H, C$H_A H_B$), 7.03 (d, 8 Hz, 2H, 8-H), 7.24 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.47 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.70 (d, 8 Hz, 2H, 5-H), 8.00 (d, 8 Hz, 2H, 3- or 4-H), 8.05 (d, 8 Hz, 2H, 3- or 4-H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 39.08 (*C*H$_2$), 126.72, 126.96, 127.23, 128.94, 128.96, 129.47, 133.25, 133.74 (2C), 135.86, 172.50 (*C*O). IR (evapd film, cm^{-1}): 3056 (w), 1714 (s, ν_{CO}), 1509 (w), 1410 (m), 1228 (m), 820 (m), 767 (m), 746 (w). FABMS: *m/z* 370 (M^+). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.74; H, 4.76.

(*R*)-1,1′-Binaphthyl-2,2′-diacetyl chloride, (2-ClCOCH$_2$C$_{10}$H$_6$)$_2$. In the drybox, (*R*)-1,1′-binaphthyl-2,2′-diacetic acid (1.5940 g, 4.30 mmol), PCl_5 (2.0622 g, 9.90 mmol) and a magnetic stirrer bar were charged into a 100 mL two-neck round-bottom flask. One neck was capped with a rubber septum and the other was attached to a Teflon needle valve. The flask was taken out of the drybox and toluene (25 mL) was added. The reaction mixture was stirred at room temperature under a flow of N_2 for 30 min to give a clear yellow solution. The solvent was removed *in vacuo*, and the oily residue was heated with a hot water bath (100 °C) for 1 h under dynamic vacuum to sublime away any unreacted PCl_5, yielding a thick brown oil (1.6228 g, 93%). ^{1}H NMR (C_6D_6): δ 3.49 (AB quartet, $\Delta\delta_{AB}$ = 0.06 ppm, J_{AB} = 18 Hz, 4H, C$H_A H_B$), 6.93 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.05 (d, 9 Hz, 2H, 8-H), 7.11 (d, 9 Hz, 2H, 5-H), 7.16 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.61 (d, 9 Hz, 2H, 3- or 4-H), 7.63 (d, 9 Hz, 2H, 3- or 4-H). ^{13}C{^{1}H} NMR (C_6D_6): δ 51.29 (*C*H$_2$), 126.84, 127.33, 127.83, 128.68, 128.84, 129.71, 130.06, 133.37, 133.82, 135.69, 171.99 (*C*O). IR (evapd film, cm^{-1}): 3057 (w), 2916 (w), 1790 (s, ν_{CO}), 1595 (w), 1509 (w),

1398 (w), 1361 (w), 1330 (w), 1308 (w), 1223 (w), 1187 (w), 1145 (w), 1023 (w), 980, (m), 959 (m), 927 (w), 878 (w), 834 (w), 803 (w), 773 (m), 742 (w), 714 (m), 665 (w). HRMS (FAB): Calcd. for $C_{24}H_{16}Cl_2O_2$ (M^+): 406.0527. Found: 406.0507.

(*R*)-1,1′-Binaphthyl-2,2′-bis-(4-*p*-tolylbutane-2,4-dione), ($C_{10}H_6$-$CH_2COCH{=}C(OH)C_6H_4$-*p*-$CH_3)_2$, (*R*)-Tol$_2$BobbinapH$_2$. In the drybox, a solution of (*R*)-1,1′-binaphthyl-2,2′-diacetyl chloride (1.2487 g, 3.07 mmol) in 20 mL of ether was prepared in a 100 mL round-bottom flask sealed with a rubber septum. Into a 125 mL Erlenmeyer flask, $LiN(Si(CH_3)_3)_2$ (2.0692 g, 12.37 mmol, Aldrich), a magnetic stirrer bar and 20 mL of ether were added. 4′-Methylacetophenone (1.70 mL, 12.7 mmol, Aldrich) was added dropwise to the solution of $LiN(Si(CH_3)_3)_2$. The flask was capped with a rubber septum. The two solutions were taken out of the drybox. The enolate solution was cooled in an ice bath for 20 min. The acyl chloride solution was added dropwise to the stirring enolate solution *via* syringe, forming a cloudy yellow mixture. After stirring for 5 min at 0 °C, the mixture was suction filtered in the air to isolate a yellow precipitate, which was washed with 3 × 10 mL ice-cold ether and transferred into a 250 mL round-bottom flask. The volume of the filtrate was reduced to about 5 mL, cooled in an ice bath for 10 min, filtered and washed as described above, and combined with the first crop of solid. The solid was digested by stirring with 50 mL 18% HCl and 50 mL benzene until it had completely dissolved. The mixture was transferred into a separatory funnel, and the aqueous layer was discarded. The clear orange organic layer was washed with 50 mL saturated $NaHCO_3$, dried over $MgSO_4$, filtered and stripped down on a rotary evaporator, yielding an orange residue. The residue was redissolved in 30 mL of ether, and the product crystallized upon standing at 10 °C overnight. After filtration and washing with 2 × 10 mL ice-cold ether, the product was obtained as a light beige solid. The filtrate was stripped down on a rotary evaporator, and the purification step was repeated until no more of the product precipitated out to give a combined yield of 1.3034 g (70%). ^{1}H NMR (C_6D_6): δ 1.98 (s, 6H, CH_3), 3.43 (AB quartet, $\Delta\delta_{AB}$ = 0.04 ppm, J_{AB} = 15 Hz, 4H, CH_AH_B), 5.49 (s, 2H, COC*H*CO), 6.85 (d, 9 Hz, 4H, Tol 3,5-H), 6.93 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.16 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.24 (d, 8 Hz, 2H, 8-H), 7.56 (d, 9 Hz, 4H, Tol 2,6-H), 7.67 (d, 8 Hz, 2H, 3- or 4-H), 7.68 (d, 8 Hz, 2H, 3- or 4-H), 7.77 (d, 8 Hz, 2H, 5-H), 16.75 (s, 2H, O*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.71 (*C*H$_3$), 44.41 (*C*H$_2$), 97.32 (CO*C*HCO), 126.51, 127.20, 127.39, 127.84, 128.67, 129.02, 129.11, 129.69, 132.71, 133.57, 133.81, 134.03, 136.12, 143.13, 183.11 (CH$_2$*C*O), 194.87 (Tol*C*O). IR (cm^{-1}): 3051 (w), 2919 (w), 1609 (s, ν_{CO}), 1568 (m), 1505 (m), 1296 (m), 1270 (m), 1184 (m), 1117 (m), 777 (w), 763 (m). FABMS: *m*/*z* 603 (M^+). Anal. Calcd for $C_{42}H_{34}O_4$: C, 83.70; H, 5.69. Found: C, 83.63; H, 5.84.

Preparation of (Tol$_2$Bobbinap)Ti complexes

(*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$. In the drybox, (*R*)-Tol$_2$-BobbinapH$_2$ (0.8700 g, 1.44 mmol) and a magnetic stirrer bar were added into a 100 mL two-neck round-bottom flask. The solid was dissolved in 30 mL of benzene. To this solution was added titanium(IV) isopropoxide (0.50 mL, 1.6 mmol). The reaction flask was capped with rubber septa, and the mixture was stirred at room temperature for 5 min. After that, one of the rubber septa was replaced with a Teflon needle valve. The flask was taken out of the drybox and affixed to a vacuum line. The solvent was removed *in vacuo*, yielding a yellow oil. The oil was taken into the drybox and triturated with 20 mL of hot hexanes. After the suspension cooled to room temperature, a light yellow solid was isolated by filtration and washed with 2 × 2 mL hexanes. Yield: 0.7902 g, 71%. ^{1}H NMR (C_6D_6): δ 1.40 (d, 6 Hz, 6H, CH(C*H*$_3$)(CH′$_3$)), 1.47 (d, 6 Hz, 6H, CH(CH$_3$)(C*H*′$_3$)), 2.10 (s, 6H, Tol C*H*$_3$), 3.04 (d, 13 Hz, 2H, C*H*H′), 3.41 (d, 13 Hz, 2H, CH*H*′), 4.60 (s, 2H, COC*H*CO), 5.19 (sept, 6 Hz, 2H, C*H*(CH$_3$)$_2$), 6.99 (d, 8 Hz, 4H, Tol 3,5-H), 7.05 (d, 8 Hz, 2H, 8-H), 7.11 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.33 (td, 7, 1 Hz, 2H, 6- or 7-H), 7.43 (d, 8 Hz, 2H, 3- or 4-H), 7.45 (d, 8 Hz, 2H, 3- or 4-H), 7.76 (d, 8 Hz, 4H, Tol 2,6-H), 7.82 (d, 8 Hz, 2H, 5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.82 (Tol *C*H$_3$), 25.43 (CH(*C*H$_3$)(*C*′H$_3$)), 25.47 (CH(CH$_3$)(*C*′H$_3$)), 46.86 (*C*H$_2$), 78.46 (*C*H(CH$_3$)$_2$), 99.84 (CO*C*HCO), 125.88, 125.97, 126.85, 127.96, 128.16, 128.60, 128.95, 131.70, 131.95, 133.25, 134.15, 135.25, 136.27, 142.12, 179.75 (CH$_2$*C*O), 189.80 (Tol*C*O). IR (nujol mull, cm^{-1}): 1598 (s), 1553 (s), 1519 (s), 1495 (s), 1318 (m), 1183 (m), 1162 (m), 1118 (s), 1017 (s), 985 (s), 850 (m), 778 (m), 759 (m). FABMS (NPOE matrix): *m*/*z* 766 (M^+), 707 ($M^+ - O^iPr$), 648 ($M^+ - 2O^iPr$). UV-Vis (CH_2Cl_2): λ_{max} 378 nm ($\varepsilon = 3.3 \times 10^4$ M^{-1} cm^{-1}), 284 nm (5.4×10^4). CD (CH_2Cl_2): 386 nm ($\Delta\varepsilon$ = +31 M^{-1} cm^{-1}), 346 (−33), 317 (−14), 286 (+54). Anal. Calcd for $C_{48}H_{46}O_6Ti$: C, 75.19; H, 6.05. Found C, 74.90; H, 5.82.

(*R*,Λ)-(Tol$_2$Bobbinap)Ti(OTf)$_2$

In the drybox, (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$ (0.3590 g, 0.47 mmol), 10 mL of benzene and a magnetic stirrer bar were added into a scintillation vial. Trimethylsilyl trifluoromethanesulfonate (0.25 mL, 1.38 mmol) was added, immediately forming a red solution. The vial was capped tightly, taken out of the drybox and heated 1 d in a 50 °C oil bath. The mixture was taken into the drybox and layered with 10 mL hexanes. A red precipitate formed after standing at room temperature overnight. The solid was isolated by decantation, washed with 2 × 2 mL hexanes and dried 1 h under vacuum to yield 0.4283 g (97%) of the bis(triflate) complex. ^{1}H NMR ($CDCl_3$): δ 2.49 (s, 6H, Tol C*H*$_3$), 3.32 (d, 14 Hz, 2H, C*H*H′), 3.61 (d, 14 Hz, 2H, CH*H*′), 4.87 (s, 2H, COC*H*CO), 7.26 (d, 8 Hz, 2H, 3- or 4-H), 7.31 (d, 8 Hz, 4H, Tol 3,5-H), 7.51 (m, 4H, 7- and 8-H), 7.61 (d, 8 Hz, 4H, Tol 2,6-H), 7.65 (d, 8 Hz, 2H, 3- or 4-H), 7.67 (m, 2H, 6-H), 8.02 (d, 8 Hz, 2H, 5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.33 (Tol *C*H$_3$), 44.60 (*C*H$_2$), 107.52 (CO*C*HCO), 125.72, 127.25, 128.06, 128.36, 128.49, 129.82, 130.03, 130.30, 131.11, 131.56, 133.58, 133.90, 135.47, 148.11, 184.68 (*C*O), 189.30 (*C*O); *C*F$_3$ not observed. ^{19}F NMR ($CDCl_3$): δ −77.28. IR (nujol mull, cm^{-1}): 1607 (w), 1526 (s), 1365 (s), 1318 (m), 1284 (w), 1238 (w), 1186 (s), 982 (m), 810 (w), 765 (w), 736 (w).

(*R*,Λ,*R*,*R*)-(Tol$_2$Bobbinap)Ti(Taddol)

In the drybox, a scintillation vial was charged with (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$ (0.2238 g, 0.29 mmol), (*R*,*R*)-TaddolH$_2$ (0.2061 g, 0.44 mmol), benzene (10 mL) and a magnetic stirrer bar. The vial was capped tightly and heated in a 75 °C oil bath overnight. The clear brown solution was opened to the air and the volatiles removed on a rotary evaporator. The yellow residue

was redissolved in 5 mL benzene and then diluted to three times its initial volume with hexanes, while stirring, forming a yellow precipitate. The suspension was kept at 10 °C overnight, filtered and washed with 2 × 2 mL hexanes, giving a bright yellow solid (0.1950 g, 60%). ^{1}H NMR (C_6D_6): δ 0.91 (s, 6H, C(CH_3)$_2$), 2.16 (s, 6H, Tol CH_3), 3.02 (d, 13.5 Hz, 2H, CHH′), 3.34 (d, 13.5 Hz, 2H, CHH′), 4.49 (s, 2H, COCHCO), 5.84 (s, 2H, Taddol OCH), 6.80 (td, 7, 1.5 Hz, 2H, 6- or 7-H), 6.99 (d, 7.5 Hz, 4H, Tol 3,5-H), 7.02 (d, 8 Hz, 2H, 3- or 4-H), 7.04 (d, 8 Hz, 2H, 3- or 4-H), 7.18 (m, 12H, Taddol m-, p-C_6H_5), 7.32 (td, 7, 1.5 Hz, 2H, 6- or 7-H), 7.45 (d, 8 Hz, 2H, 8-H), 7.52 (d, 7.5 Hz, 4H, Tol 2,6-H), 7.82 (d, 8 Hz, 2H, 5-H), 8.02 (d, 8 Hz, 4H, Taddol o-C_6H_5), 8.16 (d, 8 Hz, 4H, Taddol o-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.86 (Taddol CH$_3$), 28.13 (Tol CH$_3$), 46.91 (CH$_2$), 84.16 (Taddol OCH), 97.13 (Taddol CPh$_2$OTi), 101.29 (COCHCO), 111.44 (Taddol OC(CH$_3$)$_2$O), 126.41, 126.44, 127.10, 127.24, 127.37, 127.59, 127.81, 128.18, 128.48, 128.92, 128.96, 129.44, 130.63, 132.48, 132.64, 133.88, 134.73, 135.82, 136.68, 142.56, 144.43, 149.03, 181.33 (CO), 191.34 (CO). IR (evapd film, cm^{-1}): 3055 (w), 3024 (w), 2983 (w), 2921 (w), 1593 (m), 1561 (m), 1549 (w), 1518 (s), 1495 (s), 1447 (w), 1429 (w), 1411 (w), 1367 (s), 1321 (m), 1306 (w), 1287 (w), 1241 (w), 1215 (w), 1186 (m), 1164 (m), 1118 (m), 1097 (m), 1082 (m), 1070 (m), 1020 (m), 984 (w), 886 (m), 823 (w), 796 (w), 782 (m), 762 (m), 729 (m), 699 (m). FABMS: m/z 1113 (M + H$^+$). UV-Vis (CH_2Cl_2): λ_{max} 382 nm ($\varepsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}), 290 (6.4×10^4). CD (CH_2Cl_2): 384 nm ($\Delta\varepsilon$ = +31 M^{-1} cm^{-1}), 338 (–16), 312 (–17), 284 (+36). Anal. Calcd for $C_{73}H_{60}O_8Ti$: C, 78.77; H, 5.43. Found: C, 78.70; H, 5.24.

(*R*,Λ,*S*,*S*)-(Tol$_2$Bobbinap)Ti(Taddol)

This compound was prepared by the same procedure described for (*R*,Λ,*R*,*R*)-(Tol$_2$Bobbinap)Ti(Taddol) using (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$ (0.4062 g, 0.53 mmol) and (*S*,*S*)-TaddolH$_2$ (0.3725 g, 0.79 mmol). Yield: 0.2547 g, 43%. ^{1}H NMR (C_6D_6): δ 0.87 (s, 6H, C(CH_3)$_2$), 2.19 (s, 6H, Tol CH_3), 3.06 (d, 13.5 Hz, 2H, CHH′), 3.42 (d, 13.5 Hz, 2H, CHH′), 4.68 (s, 2H, COCHCO), 5.90 (s, 2H, Taddol OCH), 6.81 (td, 7, 1.5 Hz, 2H, 6- or 7-H), 6.88 (d, 7.5 Hz, 4H, Tol 3,5-H), 6.89 (td, 7, 1.5 Hz, 2H, 6- or 7-H), 6.97 (d, 8 Hz, 2H, 3- or 4-H), 7.00 (d, 8 Hz, 2H, 3- or 4-H), 7.21 (m, 12H, Taddol m-, p-C_6H_5), 7.23 (d, 7.5 Hz, 4H, Tol 2,6-H), 7.40 (d, 8 Hz, 2H, 8-H), 7.75 (d, 8 Hz, 2H, 5-H), 7.77 (d, 8 Hz, 4H, Taddol o-C_6H_5), 8.26 (d, 8 Hz, 4H, Taddol o-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.92 (Taddol CH$_3$), 28.19 (Tol CH$_3$), 47.08 (CH$_2$), 83.19 (Taddol OCH), 96.73 (Taddol CPh$_2$OTi), 101.07 (COCHCO), 111.20 (Taddol OC(CH$_3$)$_2$O), 126.27, 126.40, 127.13, 127.39, 127.42, 127.50, 128.55, 128.81, 128.87, 128.92, 129.71, 130.27, 132.18, 132.57, 133.85, 134.15, 135.88, 136.60, 142.60, 144.94, 149.08, 180.51 (CO), 191.23 (CO); one aromatic carbon is not observed. IR (evapd film, cm^{-1}): 3054 (w), 3034 (w), 2990 (w), 2919 (w), 1593 (m), 1561 (m), 1547 (w), 1519 (s), 1496 (s), 1446 (w), 1412 (w), 1368 (m), 1320 (m), 1306 (w), 1243 (w), 1215 (w), 1184 (m), 1164 (m), 1120 (m), 1098 (w), 1074 (m), 1021 (m), 986 (m), 889 (m), 822 (w), 799 (m), 782 (w), 762 (w), 728 (w), 697 (m), 650 (w), 640 (w), 628 (w). FABMS: m/z 1113 (M + H$^+$). UV-Vis (CH_2Cl_2): λ_{max} 379 nm ($\varepsilon = 3.1 \times 10^4$ M^{-1} cm^{-1}), 287 (6.4×10^4). CD (CH_2Cl_2): 372 nm ($\Delta\varepsilon$ = +73 M^{-1} cm^{-1}), 336 (–14), 303 (–26). Anal. Calcd for $C_{73}H_{60}O_8Ti$: C, 78.77; H, 5.43. Found: C, 77.67; H, 5.17.

X-Ray crystallography

Crystals of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) were grown by slow evaporation from ether, while crystals of (*R*,Λ)-(Bobbinap)Ti(O^{i}Pr)$_2$ were obtained from hexanes and those of (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol) were grown from dichloromethane/hexane. Crystals of (Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$ deposited from a reaction of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) with HOTf in $CDCl_3$. In each case, the crystal to be analyzed was placed in inert oil and transferred to the tip of a glass fiber in the cold N_2 stream of a Bruker Apex CCD diffractometer (T = 100 K). Data were reduced, correcting for absorption and decay, using the program SADABS. The structures were solved using direct methods, and all nonhydrogen atoms were refined anisotropically. The proper absolute configurations of the three chiral crystals were confirmed by refining the Flack x parameter[9] and in all cases agreed with the absolute configurations of the starting materials used in the preparations. Hydrogen atoms were located on difference maps and refined isotropically. Calculations used SHELXTL (Bruker AXS),[10] with scattering factors and anomalous dispersion terms taken from the literature.[11] Further details about the structures are in Table 1.

Results and discussion

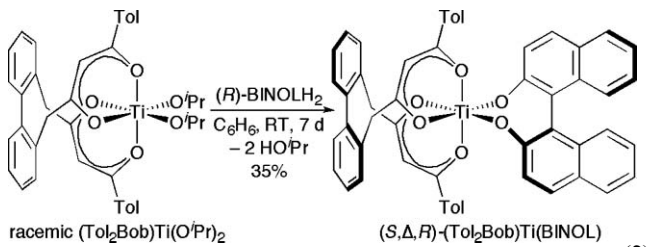
Resolution of the (Tol$_2$Bob)Ti fragment through formation of its binaphtholate

The (dike)$_2$Ti^{IV} fragment shows a very strong ability to discriminate between the enantiomers of 1,1′-bi-2-naphtholate (BINOL^{2-}), with only the (Δ,*R*)/(Λ,*S*) diastereomer of (dike)$_2$Ti(BINOL) observable by NMR spectroscopy.[3] The same diastereomer has also been observed in the solid state in (dike)$_2$Ti(2,2′-biphenolate) complexes.[12] In simple (dike)$_2$Ti(BINOL) complexes, the highly fluxional (dike)$_2$Ti fragment can respond to the configuration of the bound binaphtholate to adopt the lower-energy (matched) configuration. We hypothesized that the much more geometrically constrained linked diketonate fragment (Tol$_2$Bob)Ti would form both a matched and a mismatched diastereomer with BINOL, which could in principle be separated. Use of the commercially available optically active BINOL would then result in resolution of the (Tol$_2$Bob)Ti fragment.

In fact, racemic (Tol$_2$Bob)Ti(O^{i}Pr)$_2$ reacts slowly (~3 d at RT in C_6D_6) with optically active BINOLH$_2$ to give a mixture of products. The most abundant product is a single diastereomer of chelated (Tol$_2$Bob)Ti(BINOL). The majority of the remaining material appears to be monodentate compounds (Tol$_2$Bob)Ti(O^{i}Pr)(BINOL-H), as judged by the presence of both isopropyl signals and signals due to unsymmetrical Tol$_2$Bob and BINOL groups in the *in situ* ^{1}H NMR spectra of reaction mixtures. Reaction with 0.5 equiv. optically active BINOLH$_2$ results in formation of almost 50% of the chelated BINOL complex, with about 50% remaining diisopropoxide complex and only traces of monodentate BINOL complexes by ^{1}H NMR. The air-stable red binaphtholate chelate can be separated from the other materials by either column chromatography or fractional crystallization from benzene to give a pure single isomer in 35% isolated yield (70% based on BINOLH$_2$) (eqn (2)).

Table 1 X-Ray crystallographic details for (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL), (Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$, (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol) and (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$

	(*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL)	(Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$	(*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol)	(*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$
Molecular formula	$C_{50}H_{40}O_6Ti$	$C_{38}H_{28}D_2Cl_6F_6O_{10}S_2Ti$	$C_{65}H_{56}O_8Ti$	$C_{48}H_{46}O_6Ti$
Formula weight	832.76	1087.34	1013.00	766.75
T/K	100(2)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Triclinic	Triclinic	Monoclinic
Space group	$P4_32_12$	$P\bar{1}$	$P1$	$P2_1$
Total data collected	117 265	93 398	21 338	37 130
No. of indep reflns.	6907	14 774	11 051	9848
R_{int}	0.0424	0.0417	0.0226	0.0233
Obsd refls [$I > 2\sigma(I)$]	6167	11437	10542	9182
a/Å	13.8132(3)	11.1948(5)	9.1257(3)	11.6568(3)
b/Å	13.8132(3)	14.8069(7)	11.5661(4)	7.8240(2)
c/Å	21.5907(9)	16.0008(8)	13.5882(5)	21.7522(6)
α/°	90	62.997(2)	65.765(2)	90
β/°	90	71.233(3)	74.173(2)	92.5330(16)
γ/°	90	78.832(3)	87.031(2)	90
V/Å^3	4119.6(2)	2233.95(18)	1255.28(8)	1981.92(9)
Z	4	2	1	2
μ/mm^{-1}	0.262	0.724	0.231	0.266
Crystal size/mm	0.49 × 0.23 × 0.20	0.28 × 0.18 × 0.05	0.25 × 0.21 × 0.11	0.29 × 0.14 × 0.13
No. refined params	356	698	891	680
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0361, 0.0939	0.0428, 0.1008	0.0283, 0.0731	0.0271,0.0685



(2)

Based on previous studies, it was expected that the matched diastereomer of the compound formed from (*R*)-BINOL would have the Δ configuration at titanium,[3] and that the Δ configuration at titanium would correspond to the (*S*) configuration of the biphenyl backbone of the Tol$_2$Bob ligand.[5] X-Ray crystallography confirms that the chelated compound is indeed the predicted isomer, (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) (Fig. 1, Tables 1 and 2). The compound crystallizes in the chiral tetragonal space group $P4_32_12$ and has crystallographically required C_2 symmetry. Its titanium–oxygen distances are essentially identical to those shown in the unlinked diketonate-BINOL complexes (dbm)$_2$Ti(BINOL) and (^{t}BuCOCHCO^{t}Bu)$_2$Ti(BINOL) (average Ti–BINOL 1.863(11) Å, Ti–dike *cis* to BINOL 1.962(13) Å, Ti–dike *trans* to BINOL 2.015(16) Å).[3] The aryloxide–titanium distances in the chelated BINOL derivatives are perceptibly longer, and the *trans* effect perceptibly smaller, than in analogous complexes of monodentate aryloxides such as (acac)$_2$Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$ (Ti–OAr 1.834(5) Å, *cis*-Ti–O 1.985(5) Å, *trans*-Ti–O 2.046(5) Å)[13] or (^{t}Bu$_2$Bob)Ti(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$ (Ti–OAr 1.8173(11) Å, *cis*-Ti–O 1.9685(10) Å, *trans*-Ti–O 2.0808(11) Å).[5] These differences may be attributed to the poorer π donation possible from the chelating BINOL ligand compared to monodentate aryloxides. While Ti–OAr distances in aryloxides are not correlated with Ti–O–C angles for complexes that display the usual obtuse angles observed in monodentate aryloxides (140–180°),[14] the very acute angles imposed by the nonplanar seven-membered chelate (Ti–O–C = 121.82(8)°) interfere significantly with the ability of the in-plane oxygen lone pair to donate to the metal center.[15]

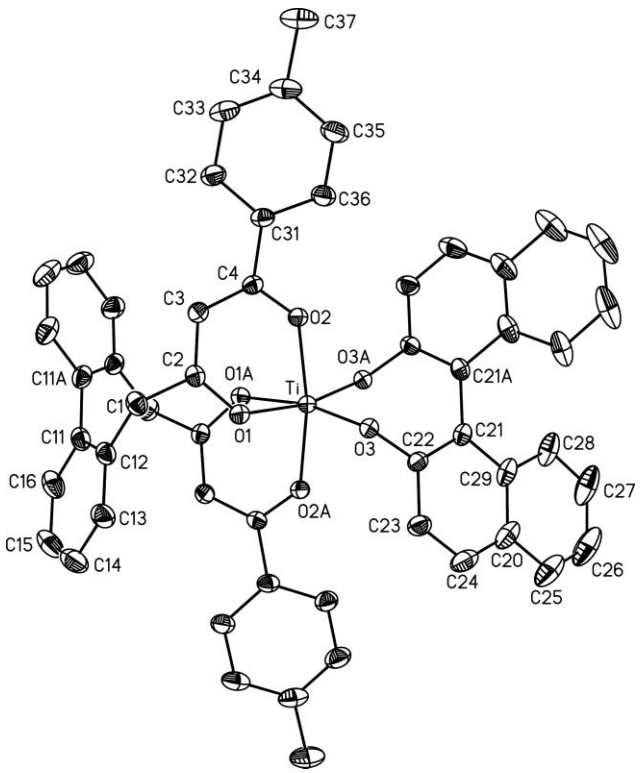


Fig. 1 Thermal ellipsoid plot of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL). Hydrogen atoms are omitted for clarity.

The enhanced stability of the (*S*,Δ,*R*) diastereomer of (Tol$_2$Bob)Ti(BINOL) is consistent with literature precedent and has been justified on electronic grounds.[3] However, the absolute inability to observe significant amounts of the (*R*,Λ,*R*) diastereomer is puzzling. Apparently the poorer π bonding in this diastereomer outweighs the entropic benefit of the chelate effect, making the

Table 2 Selected bond distances (Å) and angles (°) in (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL), (Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$, (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol) and (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)

	(*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL)	(Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$	(*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol)	(*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$
Ti–O1	2.0044(10)	1.9279(12)	2.0304(11)	2.0549(9)
Ti–O2	1.9808(9)	1.9140(11)	2.0002(11)	2.0148(10)
Ti–O3	1.8682(10)	1.9190(12)	2.0604(11)	2.1342(9)
Ti–O4		1.9073(11)	1.9611(11)	1.9983(10)
Ti–O5		1.9940(12)	1.8014(10)	1.7811(10)
Ti–O6		1.9906(12)	1.7880(10)	1.7930(9)
O1–Ti–O1a	84.23(6)			
O1–Ti–O2	82.49(4)	85.43(5)	81.71(4)	83.08(4)
O1–Ti–O3	93.15(4)	87.24(5)	81.09(4)	79.01(4)
O1–Ti–O2a	89.72(4)			
O1–Ti–O3a	168.69(4)			
O1–Ti–O4		89.23(5)	88.04(5)	84.42(4)
O1–Ti–O5		176.02(5)	166.98(4)	167.77(4)
O1–Ti–O6		91.05(5)	96.35(5)	93.83(4)
O2–Ti–O2a	169.51(6)			
O2–Ti–O3	100.87(4)	87.14(5)	87.54(4)	81.23(4)
O2–Ti–O3a	86.50(4)			
O2–Ti–O4		171.21(5)	167.27(4)	161.38(4)
O2–Ti–O5		90.85(5)	90.46(5)	92.75(4)
O2–Ti–O6		96.62(5)	95.80(5)	97.38(4)
O3–Ti–O3a	91.47(6)			
O3–Ti–O4		85.63(5)	83.41(4)	82.89(4)
O3–Ti–O5		94.01(5)	88.24(4)	89.01(4)
O3–Ti–O6		175.74(5)	175.48(5)	172.81(4)
O4–Ti–O5		94.64(5)	98.17(5)	96.63(4)
O4–Ti–O6		90.45(5)	92.81(5)	97.17(4)
O5–Ti–O6		87.95(5)	94.77(5)	98.12(4)
Ti–O3–C22	121.82(8)			
Ti–O5–X		137.17(7)[a]	145.37(9)[b]	148.53(9)[c]
Ti–O6–Y		139.20(8)[a]	148.65(10)[b]	137.12(9)[c]

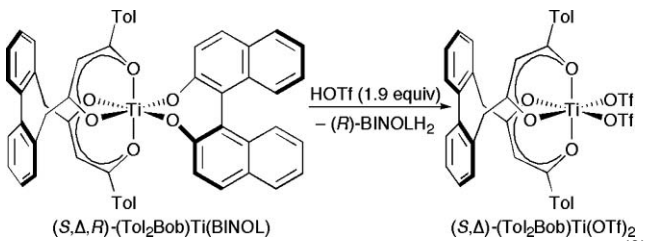
[a] X = S1, Y = S2. [b] X = C51, Y = C54. [c] X = C52, Y = C62.

chelated compound unstable with respect to alcoholysis under the reaction conditions used. A similar effect was seen in the reaction of (Fc$_2$Bob)Ti(O^{i}Pr)$_2$ with catechol, where the limited π donation from the catechol favors formation of the monodentate catechol complex (Fc$_2$Bob)Ti(OC$_6$H$_4$-2-OH)$_2$, and the chelate complex is again unobservable.[16]

The binaphtholate ligand can be cleaved from (Tol$_2$Bob)Ti(BINOL), for example by treatment with trifluoromethanesulfonic acid to give (Tol$_2$Bob)Ti(OTf)$_2$. However, if the solution is allowed to stand for an extended period, particularly in the presence of excess acid, then the product racemizes. For example, crystals of *racemic* (Tol$_2$Bob)Ti(OTf)$_2$·2CDCl$_3$ deposit upon treatment of optically active (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) with HOTf in CDCl$_3$ (Fig. 2), although of course the (*S*,Δ)/(*R*,Λ) relative configuration of the biphenyl and titanium centres is retained, as it is in all R$_2$Bob and related compounds observed to date.[5,6,16]

The short Ti–diketonate bonds in (Tol$_2$Bob)Ti(OTf)$_2$ (Table 2) suggest an extremely electron-poor titanium centre in this compound. For example, the axial diketonate Ti–O bonds are shorter than the corresponding bonds in most other bis(diketonate) compounds, with the only rivals being the 1.905–1.928 Å bonds found in bis(diketonate) titanium chlorides.[17] The equatorial Ti–O bonds *trans* to triflate are the shortest known in (dike)$_2$Ti compounds, shorter even than the 1.944 Å bond *trans* to ether in the cationic etherate [(Tol$_2$Bob)Ti(O^{i}Pr)(OEt$_2$)]BAr$_F$.[5] The titanium–triflate distances are typical of those seen in other titanium triflates in oxygen-rich environments.[18]

If a slightly deficient amount of HOTf is used and the product precipitated promptly with hexane, then optically pure (*S*,Δ)-(Tol$_2$Bob)Ti(OTf)$_2$ can be prepared from the binaphtholate complex (eqn (3)), although the triflate is contaminated by traces (~2%) of the binaphtholate. The optical purity can be judged by reaction of the compound with (*R*,*R*)-TaddolH$_2$ in the presence of Et$_3$N, which gives diastereomerically pure (*S*,Δ,*R*,*R*)-(Tol$_2$Bob)Ti(Taddol) (see below). Once isolated, (*S*,Δ)-(Tol$_2$Bob)Ti(OTf)$_2$ has modest optical stability. Upon heating for 2 d at 51 °C in CDCl$_3$, the optical purity decreases to 38% ee (as judged by quenching with (*R*,*R*)-TaddolH$_2$/Et$_3$N), giving an approximate half-life for racemization of 34 h at 324 K. Since this reaction may be catalyzed by traces of protic impurities in the solvent, this represents a lower limit of the intrinsic optical stability of (Tol$_2$Bob)Ti(OTf)$_2$.



(3)

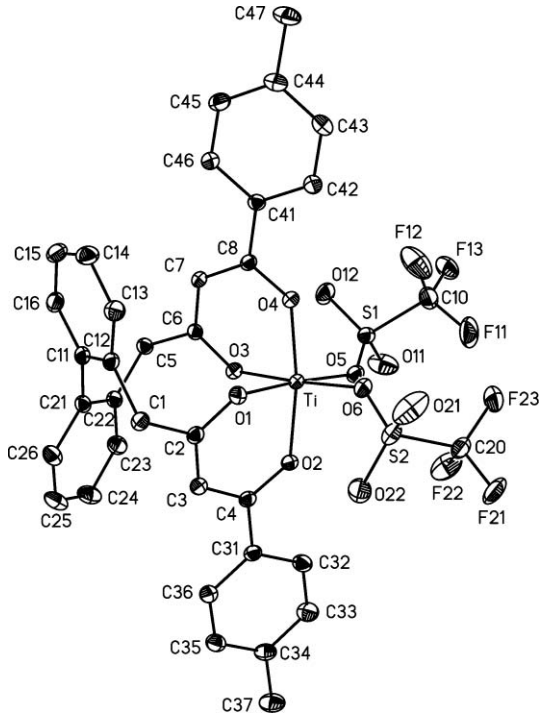


Fig. 2 Thermal ellipsoid plot of $(Tol_2Bob)Ti(OTf)_2{\cdot}2CDCl_3$. Hydrogens and solvent of crystallization are omitted for clarity. The crystal is racemic, with the (R,Λ) isomer shown.

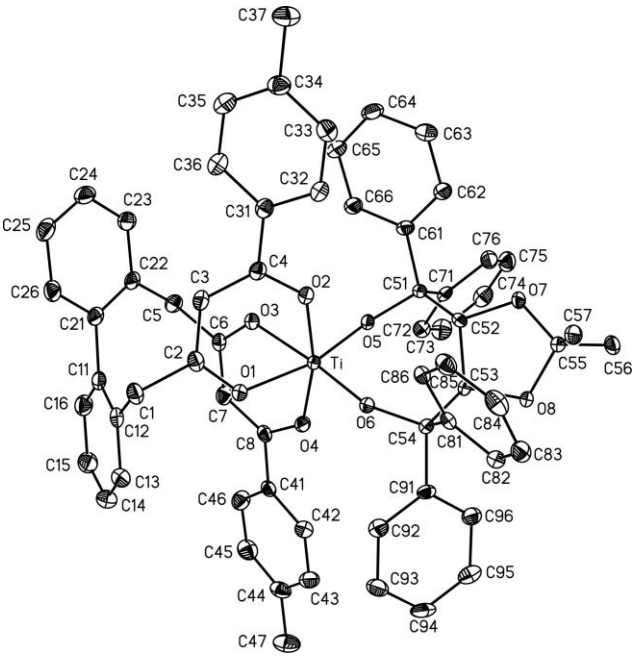


Fig. 3 Thermal ellipsoid plot of (S,Δ,R,R)-$(Tol_2Bob)Ti(Taddol)$. Hydrogens are omitted for clarity.

The $(Tol_2Bob)Ti$ fragment can undergo alcohol exchange reactions with retention of configuration at titanium. For example, heating (S,Δ,R)-$(Tol_2Bob)Ti(BINOL)$ with (R,R)-$TaddolH_2$ produces principally one diastereomer, (S,Δ,R,R)-$(Tol_2Bob)Ti(Taddol)$, which can be isolated in pure form after recrystallization and whose stereochemistry was verified by X-ray crystallography (Fig. 3). The metrical data for the complex (Table 2) are unexceptional, although there is a slight distortion from ideal C_2 symmetry, particularly in the titanium–diketonate distances, probably caused by packing forces in the crystal. The structure of the unlinked bis(diketonate)titanium(IV) complex $(acac)_2Ti(Taddol)$ has been reported and appears to be the (Λ,R,R) isomer in the solid, though no details were provided.[19]

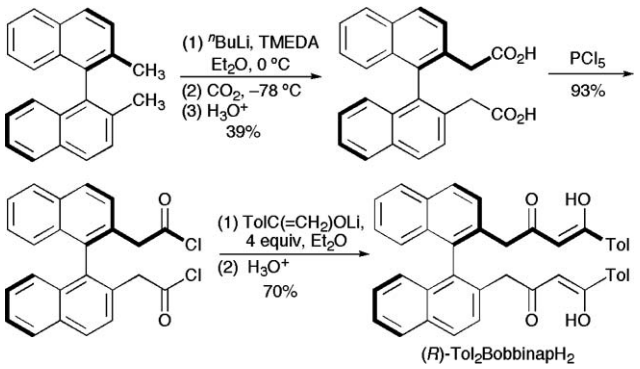
Examination of NMR spectra of the crude reaction mixture does reveal small amounts (~5%) of the other diastereomer, whose NMR properties can be verified by preparation of its enantiomer from (S,S)-$TaddolH_2$ and (S,Δ,R)-$(Tol_2Bob)Ti(BINOL)$. Thus, the $(Tol_2Bob)Ti$ fragment racemizes slightly under these conditions. Other protic reagents also cause racemization; for example, heating (S,Δ,R)-$(Tol_2Bob)Ti(BINOL)$ in neat 2-propanol (74 °C, 1 wk) produces $(Tol_2Bob)Ti(O^iPr)_2$ in modest yield and in completely racemic form.

Overall, $(Tol_2Bob)TiX_2$ complexes are vastly more stable to racemization than unlinked $(dike)_2TiX_2$ complexes. For example, $(acac)_2TiCl_2$ racemizes with a rate constant (extrapolated to 324 K) of 1400 s^{-1},[4a] about 2×10^8 times faster than $(Tol_2Bob)Ti(OTf)_2$. The enhanced optical stability can be rationalized on the basis of the tight coupling between the biaryl and the metal-centred chirality: even if epimerization at titanium takes place, the configuration at the biphenyl group is retained, effectively promoting re-epimerization at titanium to restore the (much more stable) original diastereomer. The sensitivity of the optical (but not chemical) stability to protic reagents suggests that such compounds reversibly protonolyze one arm of the bis(diketonate) ligand, which readily dissociates from the titanium, rotates around the biaryl bond with a much lower barrier, and recoordinates to the titanium.

Given the facile racemization of the $(Tol_2Bob)Ti$ fragment in the presence of alcohols, one would expect that reaction of $(Tol_2Bob)Ti(O^iPr)_2$ with 1 equiv. optically active $BINOLH_2$ to give high yields of the more stable (S,Δ,R)-$(Tol_2Bob)Ti(BINOL)$, since epimerization of (R,Λ)-(Tol_2Bob) would be driven by formation of the more thermodynamically stable binaphtholate.[20] Unfortunately, such a thermodynamic resolution has not yet been achieved in practice. Yields of (S,Δ,R)-$(Tol_2Bob)Ti(BINOL)$ do not exceed 50% even in the presence of excess (R)-$BINOLH_2$ or at extended reaction times.

Optically active complexes of bis(methylene)binaphthyl bridged bis(β-diketonates): the Bobbinap ligand

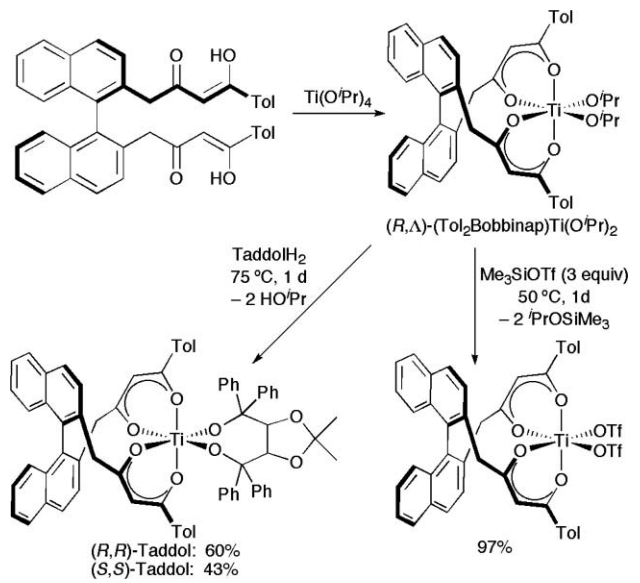
Because of the sensitivity of the optical stability of the $(Tol_2Bob)Ti$ fragment to protic media, we sought an alternative strategy to produce an enantiomerically pure bis(diketonate) fragment. Given the tight coupling between the configuration of the bis(methylene)biphenyl linker and the configuration at titanium observed in all $(R_2Bob)Ti$ complexes, it seemed reasonable that a bis(diketonate) ligand bridged by an optically stable 2,2′-bis(methylene)-1,1′-binaphthyl fragment would provide a suitable entry to such compounds. The preparation of this "Bobbinap" ligand is outlined in Scheme 1. Optically active (R)-2,2′-dimethylbinaphthyl (prepared in two steps from commercially available (R)-$BINOLH_2$[7]) is lithiated with ^{n}BuLi/TMEDA as initially described for the racemic compound by Raston and coworkers[8a] and more recently applied to the optically active



Scheme 1 Synthesis of $Tol_2BobbinapH_2$.

material.[8b] Carboxylation of the crystalline organolithium provides the diacid, which is converted to the acyl chloride using PCl_5. Formation of the bis(diketone) is achieved by Claisen condensation with 4 equiv. of the lithium enolate of 4′-methylacetophenone to give $Tol_2BobbinapH_2$. As we have previously observed,[5,6,16] use of two additional equivalents of the enolate as the sacrificial base is critical in working with this substrate which contains acidic α hydrogens, and precipitation of the lithium salt of the diketonate prior to workup greatly simplifies purification of the final bis(diketone).

The bis(diketone) ligand (*R*)-$Tol_2BobbinapH_2$ is readily metalated on treatment with $Ti(O^iPr)_4$ (Scheme 2). Analogous metalation of the biphenyl-bridged Tol_2BobH_2 ligand at room temperature produces a mixture of monomeric and oligomeric compounds, which require heating in the presence of excess $Ti(O^iPr)_4$ to convert to the desired monomer.[5] In contrast, the binaphthyl-bridged compound gives only monomeric product (as judged by *in situ* ^{1}H NMR spectroscopy), so metalation can be carried out at room temperature and without excess titanium. The ^{1}H NMR spectrum of $(Tol_2Bobbinap)Ti(O^iPr)_2$ is very similar to that of its biphenyl-bridged analogue, except that one of the diastereotopic methylene protons and the diketonate methine proton are shifted markedly upfield in the binaphthyl



Scheme 2 Preparation and reactivity of (R,Λ)-$(Tol_2Bobbinap)Ti(O^iPr)_2$.

complex compared to the biphenyl complex ($\Delta\delta$ = –0.35 and –0.74 ppm, respectively, in C_6D_6), suggesting that these hydrogens are in the shielding cone of the backbone naphthyl groups. NMR spectroscopy shows that only one diastereomer of the compound is present, and that isomer is confirmed to be the (R,Λ) isomer by X-ray crystallography (Table 1, Fig. 4). Bond lengths and angles in the compound are unexceptional (Table 2), although the compound shares with the Taddol complex a slight distortion from C_2 symmetry. The presence of the binaphthyl group, rather than biphenyl, in the backbone of the bridged diketonate has little effect on its structure. Indeed, despite the additional steric hindrance afforded by benzannulation, the $(Bobbinap)Ti(O^iPr)_2$ shows the *smallest* dihedral angle between the biaryl groups of any of the compounds described here (105.3(2)°, compared to 115.2(2)° in the BINOL complex, 110.4(2)° in the bis(triflate), or 114.0(2)° in the Taddol complex).

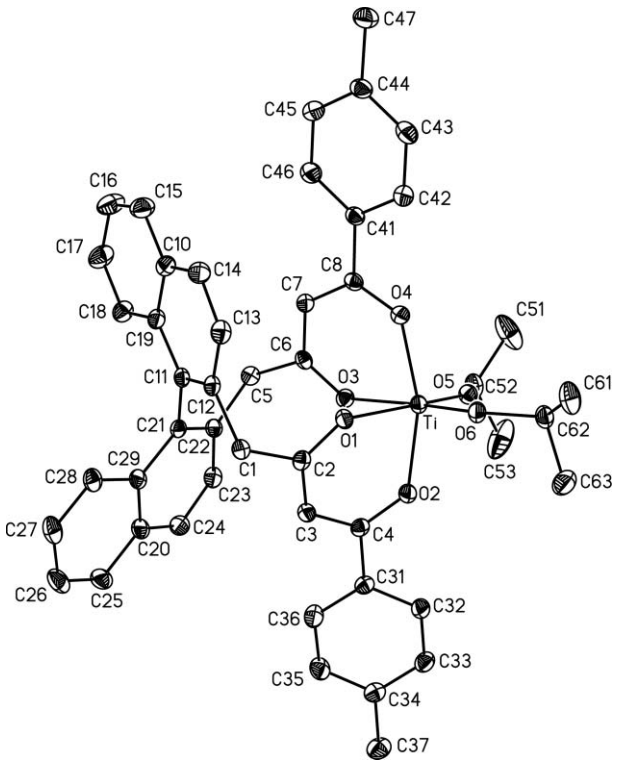


Fig. 4 Thermal ellipsoid plot of (R,Λ)-$(Tol_2Bobbinap)Ti(O^iPr)_2$. Hydrogen atoms are omitted for clarity.

The alkoxide ligands in (R,Λ)-$(Tol_2Bobbinap)Ti(O^iPr)_2$ are readily replaced by alcohol exchange. For example, the complex reacts with either (*R*,*R*)- or (*S*,*S*)-$TaddolH_2$ to form the diastereomeric chelated complexes (R,Λ,R,R)- or (R,Λ,S,S)-$(Tol_2Bobbinap)Ti(Taddol)$ (Scheme 2). In each case, monitoring the reactions *in situ* indicates that they proceed quantitatively to give only a single diastereomer, with no trace of the alternative diastereomer detectable by ^{1}H NMR spectroscopy. This confirms that the stereochemical integrity of the binaphthyl moiety has been preserved throughout the ligand synthesis, metalation, and alcohol exchange reaction. The isopropoxide groups can also be removed by treatment with trimethylsilyl triflate to produce the triflate complex (R,Λ)-$(Tol_2Bobbinap)Ti(OTf)_2$.

Circular dichroism spectroscopy of optically active bis(diketonato)titanium(IV) complexes

The availability of optically active titanium(IV) bis(diketonate) complexes allows for the first time an investigation of their chiroptical properties. The circular dichroism spectrum of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) displays a feature with a negative Cotton effect at 370 nm associated with an optical band at 388 nm, and two peaks with positive Cotton effects at 321 and 288 nm associated with the UV feature at 292 nm (Fig. 5).

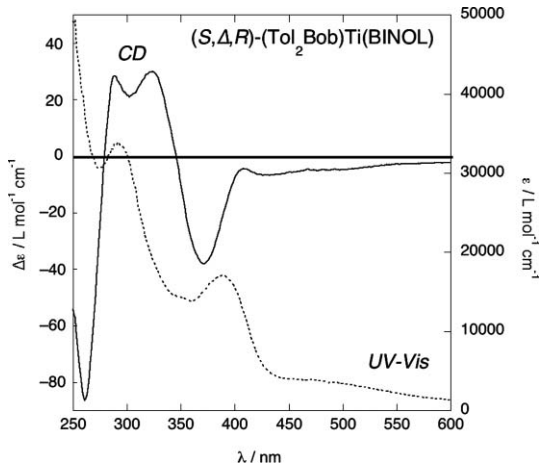


Fig. 5 UV-visible (dotted line, right axis) and CD (solid line, left axis) spectra of (*S*,Δ,*R*)-(Tol$_2$Bob)Ti(BINOL) in CH_2Cl_2.

These two optical bands have been assigned as largely diketonate π–π* in character, but with significant admixture of ligand to titanium charge transfer character.[21] The weaker negative Cotton effects in the CD at long wavelength are presumably associated with the low-energy tail of the 388 nm band discernible in the UV-visible spectrum; similar splitting of this band has been observed previously in halide complexes such as (Tol$_2$Bob)TiCl$_2$[16] and is not observed in alkoxide complexes. There is also a short-wavelength feature with strongly negative ellipticity at 261 nm.

The same general features are also apparent in the CD spectra of (*S*,Δ)-(Tol$_2$Bob)Ti(Taddol) complexes (Fig. 6), and in mirror image in the (*R*,Λ)-(Tol$_2$Bobbinap)Ti alkoxides (Fig. 7). Notably, the signs of the CD features are unaffected by the configuration of the Taddol ligand (and are similar in the isopropoxide complex as well). There are noticeable differences among the sets of spectra. For example, the splitting of the positive band at ~310 nm that was evident in the spectrum of the binaphtholate complex is much less apparent in the spectra of the (Tol$_2$Bob)Ti(Taddol) complexes, although the presence of two bands is discernible in the unsymmetrical peak shape of the feature. Likewise, the negative peak at high energy is not as distinct in the (Tol$_2$Bob)Ti(Taddol) complexes. Conversely, the splitting of the medium energy band is very apparent in the Bobbinap complexes, and the high-energy feature is also prominent (now at positive Δε, as expected for these Λ-configured complexes), and are shifted ~20 nm to longer wavelength. (Curiously, there is no corresponding shift in the UV-visible spectra, which are very similar between the Tol$_2$Bob and Tol$_2$Bobbinap complexes.) The intensities of the bands vary as well; for example, the (*S*,Δ,*R*,*R*)/(*R*,Λ,*S*,*S*) complexes have long-wavelength bands that are consistently about twice as intense (and

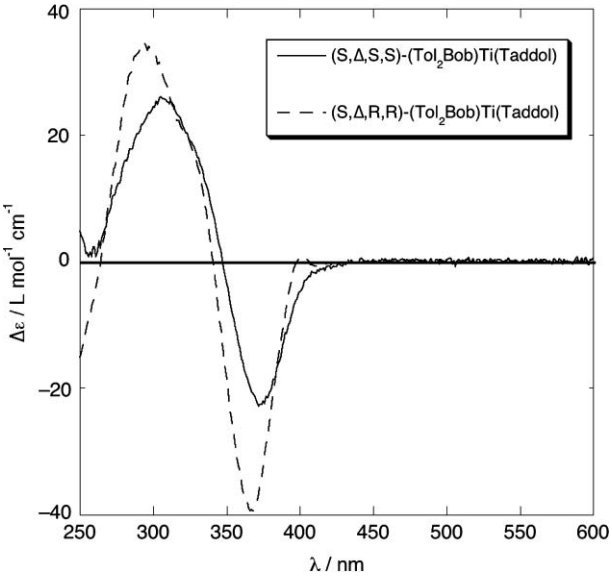


Fig. 6 Circular dichroism spectra (CH_2Cl_2) of (*S*,Δ,*S*,*S*) (solid line) and (*S*,Δ,*R*,*R*) (dashed line) isomers of (Tol$_2$Bob)Ti(Taddol).

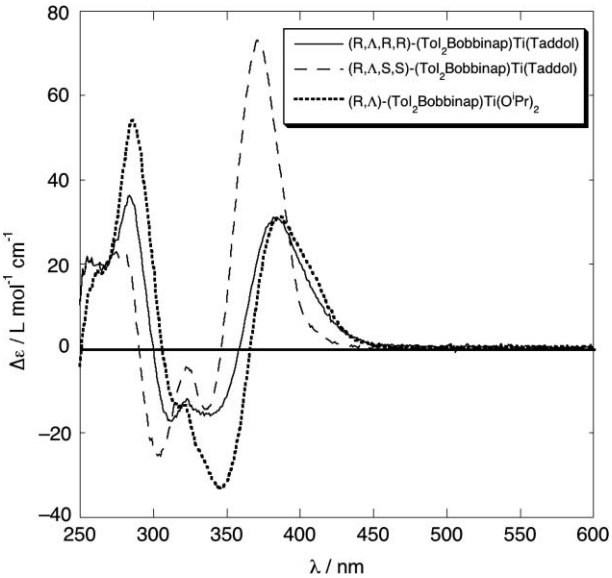


Fig. 7 Circular dichroism spectra (CH_2Cl_2) of (*R*,Λ,*R*,*R*)-(Tol$_2$Bobbinap)Ti(Taddol) (solid line), (*R*,Λ,*S*,*S*)-(Tol$_2$Bobbinap)Ti(Taddol) (dashed line), and (*R*,Λ)-(Tol$_2$Bobbinap)Ti(O^{i}Pr)$_2$ (dotted line).

peak at ~5 nm shorter wavelength) than their (*S*,Δ,*S*,*S*)/(*R*,Λ,*R*,*R*) diastereomers. But the general features of the CD spectra are sufficiently consistent to be reliable reporters on the configuration of the bis(diketonate)titanium fragment, with a negative Cotton effect at ~370 nm and a positive Cotton effect at ~320 nm indicating a Δ configuration. This could be useful in probing the ability of ligands to induce chirality on configurationally mobile (dike)$_2$Ti complexes in solution.

Conclusions

Two strategies have been implemented successfully to produce optically active bis(diketonate) complexes of titanium(IV). Both strategies rely on the high configurational stability of

2,2′-bis(methylene)biaryl-linked bis(diketonato) ("Bob") complexes of titanium, which contrasts with the fluxionality of simple bis(diketonate)titanium(IV) complexes. In the first strategy, the racemic biphenyl-bridged complex can be resolved by selective formation of the (*S*,Δ,*R*) diastereomer of (Tol_2Bob)Ti(BINOL) using optically active (*R*)-BINOL. While the binaphtholate can be removed from titanium on careful treatment with triflic acid to form optically active (Tol_2Bob)Ti($OTf)_2$, the optical stability of the compound is modest ($t_{1/2}$ for racemization = 34 h at 51 °C) and racemization is strongly accelerated in the presence of protic reagents. The second strategy builds chirality into the backbone using an optically active 2,2′-bis(methylene)-1,1′-binapthyl bridge; strong geometric coupling between the biaryl bridge enforces a Λ configuration at titanium using the (*R*)-Tol_2Bobbinap ligand. Regardless of ancillary ligation, the circular dichroism spectra show a negative ellipticity at ~370 nm and positive ellipticity at ~320 nm for the Δ isomers, with the Λ isomers showing the reverse pattern. Application of these optically active complexes in stereoselective synthesis is currently being explored.

Acknowledgements

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