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# Mononucleating Bis($\beta$-diketonate) Ligands and Their Titanium(IV) Complexes

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Novel bis($\beta$-diketones) linked by 2,2′-biphenyldiyl, 2,2′-tolandiyl, and 2,2′-bis(methylene)biphenyl moieties have been prepared. All are metalated readily by titanium(IV) isopropoxide, but the nature of the complexes formed depends on the linker structure. The biphenyl-bridged ligand gives only traces of a mononuclear complex, which is thermodynamically unstable with respect to oligomerization. The tolan-bridged ligand does form mononuclear complexes, but only as a mixture of geometric isomers. In contrast, the substituted 2,2′-bis-(2,4-dioxobutyl)biphenyl ligands, $R_2BobH_2$ ($R = {}^tBu$, *p*-Tol), react with $Ti(O^iPr)_4$ to give, initially, a mixture of monomer and oligomers, which is converted quantitatively to monomer upon heating in the presence of excess $Ti(O^iPr)_4$. Only a single relative configuration of the biphenyl and bis(chelate) titanium moieties, established by crystallography of $({}^tBu_2Bob)Ti(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2$ to be the $(R)$-$\Lambda$/$(S)$-$\Delta$ diastereomer, is observed. The kinetic and thermodynamic robustness of the $(R_2Bob)Ti$ framework is confirmed by reactions with Lewis acids. For example, $(Tol_2Bob)Ti(O^iPr)_2$ reacts with trimethylsilyl triflate or triflic acid to substitute one or both of the isopropoxide groups with triflates without any redistribution or loss of the diketonate ligands. Cationic complexes can be prepared by abstraction of triflate from $(Tol_2Bob)Ti(O^iPr)(OTf)$ with $Na[B(C_6H_3(CF_3)_2)_4]$. For example, in the presence of diethyl ether, the crystallographically characterized $[(Tol_2Bob)Ti(O^iPr)(OEt_2)][B(C_6H_3(CF_3)_2)_4]$, containing a rapidly dissociating ether ligand, is formed.

## Introduction

The $\beta$-diketonates form a versatile class of chelating ligands[1] whose use in transition metal chemistry has been appreciated for almost 120 years.[2] While octahedral tris(diketonate) complexes are probably best-known, monomeric bis(diketonate) complexes, either homoleptic complexes with divalent metals or heteroleptic $(dike)_2M(OR)_2$ complexes with transition metals such as titanium[3] or zirconium[4] or main group elements such as silicon[5] or tin,[6] are also common.

However, bis($\beta$-diketonate) ligands that form complexes in which both diketonates are bonded to the same metal center have not been previously known. Instead, linked bis(diketonates) have been used exclusively to construct dimetallic[7] or polymetallic[8] architectures. Indeed, until recently, there were no reports of any $\beta$-diketonate that was further chelated to a single metal center. We recently reported the first such complex, a titanium complex of a hydroxyphenyl-$\beta$-diketone ligand (eq 1), where the pendant phenoxide forms a 10-membered ring that is thermodynamically stable and relatively free of strain.[9]

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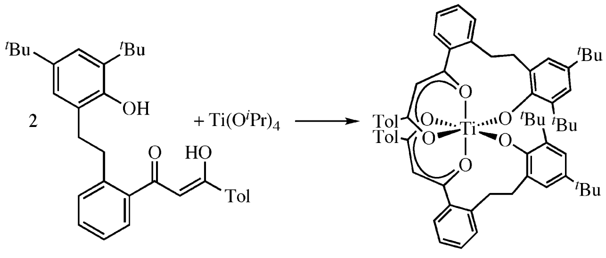

(1)

We recently demonstrated that the bis(diketonate)titanium(IV) fragment has a substantial ability to discriminate between enantiomers of chiral $\pi$-donor ligands such as 1,1′-bi-2-naphtholate by virtue of its chiral electronic structure.[10] To make practical use of this phenomenon, it would be necessary to prepare a configurationally stable (dike)$_2$Ti fragment. This poses a challenge, since known (dike)$_2$TiX$_2$ complexes are invariably observed to racemize on the NMR time scale at or below room temperature.[11] Furthermore, the coordinatively saturated octahedral bis(diketonate)titanium complexes are relatively unreactive. Achieving useful levels of reactivity would presumably require labilizing one of the sites to allow access for neutral substrates. Yet the ability to simply abstract an X ligand from a (dike)$_2$TiX$_2$ compound using a Lewis acid appeared doubtful because of the apparent lability of the diketonates.[12] Indeed, reactions with Lewis acids are reported to lead to facile ligand redistribution and isolation of coordinatively saturated tris(diketonate)titanium(IV) cations.[13]

We therefore became interested in preparing a linked bis-$\beta$-diketonate ligand. It was hoped that the additional chelation in such a tetradentate ligand would enhance binding to titanium(IV), decreasing the kinetic and thermodynamic propensity for ligand redistribution upon treatment with Lewis acids. Furthermore, such a linked structure might be more geometrically constrained and so rigidify the complex against stereomutation. Here, we report a series of bis-$\beta$-diketonate ligands spanned by linkers of varying length and structure. The 2,2′-bis(methylene)biphenyl linker, in particular, is found to give stereochemically well-defined titanium(IV) complexes of high kinetic and thermodynamic stability, allowing alkoxide abstraction by Brønsted or Lewis acids without redistribution of the diketonates.

## Experimental Section

Unless otherwise noted, all procedures were carried out on the benchtop. When necessary, chloroform and methylene chloride were dried over 4 Å molecular sieves, followed by CaH$_2$. Benzene and toluene were dried over sodium and ether, and tetrahydrofuran was dried over sodium benzophenone ketyl. 2-Propanol was dried over 4 Å molecular sieves. Sodium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (NaBAr$_F$) was prepared by a literature procedure.[14] All other reagents were commercially available and used without further purification. Routine NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts for $^1$H and $^{13}$C-{$^1$H} spectra are reported in parts per million referenced to TMS; those for $^{19}$F are reported in parts per million referenced to internal CCl$_3$F. The free $\beta$-diketones invariably appear principally as their enol forms by NMR. Variable-temperature $^1$H NMR spectra were measured on a Varian VXR-500 spectrometer. Infrared spectra were recorded as evaporated films on KBr plates (except as indicated) on a Perkin-Elmer PARAGON 1000 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 isotope envelopes; in all cases, isotope patterns were in agreement with values calculated from the molecular formulas. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ) or Canadian Microanalytical Service, Ltd. (Vancouver, BC).

**2,2′-Biphenyldicarbonyl Chloride, (2-ClCOC$_6$H$_4$)$_2$.** (2-ClCO-C$_6$H$_4$)$_2$ was prepared using phosphorus pentachloride, but under milder conditions than previously reported.[15] In the drybox, a magnetic stirbar, 2,2′-biphenyldicarboxylic acid (0.716 g, 2.95 mmol, Acros), PCl$_5$ (2.683 g, 12.9 mmol, Aldrich), and 10 mL of C$_6$H$_6$ were mixed in a 50 mL round-bottom flask, forming a gray suspension. The flask was capped with a rubber septum and stirred for 1 h at room temperature. In about 15 min, the initial suspension of reactants became a cloudy tan solution with some solid PCl$_5$ remaining. The flask was opened; the solution was filtered through a glass frit and collected in a 50 mL round-bottom flask. A Teflon needle valve was attached to the flask, which was then affixed to a vacuum line, and the solvent was completely removed. The crude brown solid was extracted with 70 mL of hot hexane in the drybox, and the hexane extract was filtered. The solvent was removed on the vacuum line to give 2,2′-biphenyldicarbonyl chloride (0.63 g, 77%) as a white solid that was stored in a drybox. $^1$H NMR (C$_6$D$_6$): $\delta$ 6.62 (dd, 7, 1 Hz, 2H, 6-H), 6.84 (td, 8, 2 Hz, 2H, 4- or 5-H), 6.90 (td, 8, 2 Hz, 2H, 4- or 5-H), 7.93 (dd, 8, 1 Hz, 2H, 3-H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 128.54, 130.70, 133.13, 133.58, 134.06, 142.77, 167.54 ($C$═O). IR (cm$^{-1}$): 1776 (s, C═O; lit. 1775),[16] 1732 (m), 1634 (s), 1595 (s), 1566 (s), 1488 (w), 1464 (w), 1409 (m, broad), 1329 (w), 1271 (w), 1251 (w), 1196 (s), 1166 (w), 1129 (w), 1110 (w), 966 (w), 894 (m), 875 (w), 778 (s), 759 (m), 748 (m), 733 (s). Anal. Calcd for C$_{14}$H$_8$Cl$_2$O$_2$: C, 60.24; H, 2.89. Found: C, 61.51; H, 3.03.

**2,2′-Bis(4,4-dimethyl-1,3-dioxopentyl)biphenyl, (${}^t$BuCOCH$_2$-COC$_6$H$_4$)$_2$ (L$^1$H$_2$).** In the drybox, a magnetic stirbar, pinacolone (0.217 g, 2.20 mmol, Aldrich), and 15 mL of THF were added to a 25 mL round-bottom flask. LiN(SiMe$_3$)$_2$ (0.731 g, 4.36 mmol, Aldrich) was added to the colorless solution, which was stirred for 5 min. This light yellow solution was slowly added, dropwise, into a 50 mL round-bottom flask containing a solution of 2,2′-biphenyldicarbonyl chloride (0.30 g, 1.07 mmol) in 10 mL of THF. The reaction mixture turned dark yellow. The flask was capped

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with a rubber septum, taken out of the drybox, and stirred for 1.5 h in a 75 °C oil bath. The dark brown reaction mixture was removed from the bath, cooled to room temperature, and poured into a separatory funnel with 50 mL of 1 M HCl and 20 mL of ether. The yellow organic layer was separated and washed with 50 mL $H_2O$. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator leaving a dark yellow residue. The thick residue was extracted with 4 × 20 mL of hexane. The hexane solutions were combined, and the solvent was removed on a rotary evaporator leaving a thick orange oil. The oil was redissolved in ~20 mL of hexane with slight heating and chromatographed on silica gel, washing the column first with pure hexane, then eluting the 2,2′-bis(4,4-dimethyl-1,3-dioxopentyl)-biphenyl with 100:1 hexane/ether. The collected fractions were combined, and the solvent was removed on a rotary evaporator leaving a white solid which was vacuum-dried overnight. Yield: 0.082 g, 18%. $^1$H NMR ($C_6D_6$): $\delta$ 0.92 (s, 18 H, $^t$Bu), 5.60 (s, 2H, COC*H*CO), 7.02 (m, 6H, aromatic protons), 7.76 (m, 2H, 3-H), 16.66 (br s, 2H, O*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 27.43 (*C*$H_3$), 39.80 (*C*$CH_3$), 98.67 (CO*C*HCO), 128.27, 129.43, 131.01, 131.55, 137.31, 141.06, 187.16 (*C*O), 201.94 (*C*O). IR ($cm^{-1}$): 2970 (s), 2938 (m), 2906 (w), 2870 (w), 1606 (s, C═O), 1587 (s), 1568 (s), 1477 (m), 1459 (m), 1438 (m), 1363 (m), 1372 (m), 1293 (m), 1248 (w), 1226 (w), 1162 (w), 1127 (w), 1042 (w), 1023 (w), 1004 (w), 955 (w), 938 (w), 850 (w), 807 (m), 766 (s), 754 (m), 740 (m). FAB-MS: *m*/*z* 407 $(M + H)^+$. Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.62; H, 7.35.

**1-(2-iodophenyl)-3-*p*-tolylpropane-1,3-dione, $(2\text{-}IC_6H_4)COCH_2\text{-}COC_6H_4\text{-}p\text{-}CH_3$.** In the drybox, $LiN(SiMe_3)_2$ (1.734 g, 10.4 mmol) was added to 20 mL of ether. This solution was slowly added, with stirring, into a 125 mL Erlenmeyer flask containing a magnetic stirbar and 4′-methylacetophenone (0.594 g, 4.43 mmol, Aldrich), forming a light yellow solution. The residual $LiN(SiMe_3)_2$ was washed with 2 × 5 mL of dry ether, and the washes were added to the reaction solution. A solution of 2-iodobenzoyl chloride (1.176 g, 4.41 mmol) in 10 mL of ether was added dropwise to the stirring lithium hexamethyldisilazide/enolate mixture, forming a pale yellow precipitate in the yellow solution. The flask was capped with a rubber septum and stirred for 7 h at room temperature; the solution color changed to light brown. The flask was opened, and the precipitate was filtered in the air on a glass frit. The pale yellow solid in the frit was washed with 2 × 10 mL of cold ether and then transferred into a separatory funnel with 30 mL of ether and washed for 10 min with 50 mL of 1 M HCl. The yellow organic layer was separated and washed with 50 mL of $H_2O$, dried over $MgSO_4$, filtered, and stripped down on a rotary evaporator, leaving a dark yellow residue. The thick residue was extracted with 4 × 20 of mL hexane, and the hexane extracts were reduced in volume to ~10 mL. Purification by column chromatography (silica gel, 100:1 hexane/ether) gave 1-(2-iodophenyl)-3-*p*-tolylpropane-1,3-dione (0.444 g, 29%) as a pale yellow solid. $^1$H NMR ($CDCl_3$): $\delta$ 2.44 (s, 3H, tolyl C*$H_3$*), 6.55 (s, 1H, COC*H*CO), 7.14 (td, 8, 2 Hz, 1H, $IC_6H_4$ H-4 or -5), 7.29 (d, 8 Hz, 2H, Tol 3,5-H), 7.44 (td, 8, 2 Hz, 1H, $IC_6H_4$ H-4 or -5), 7.53 (dd, 8 Hz, 2 Hz, 1H, $IC_6H_4$ H-3 or -6), 7.87 (d, 8 Hz, 2H, Tol 2,6-H), 7.97 (dd, 8, 2 Hz, 1H, $IC_6H_4$ H-3 or -6), 16.29 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 21.87 (tolyl *C*$H_3$), 93.26 (I−*C*), 97.61 (CO*C*HCO), 127.51, 128.34, 129.37, 129.67, 131.72, 132.14, 140.71, 142.46, 143.78, 184.27 (*C*O), 190.25 (*C*O). IR ($cm^{-1}$): 1607 (s, very broad), 1564 (s), 1499 (s), 1464 (s), 1292 (m), 1260 (m), 1226 (m), 1208 (m), 1185 (m), 1114 (w), 1098 (w), 1061 (w), 1033 (w), 1012 (s), 954 (m), 868 (m), 839 (w), 832 (w), 793 (s), 763 (s), 737 (m), 723 (w). FAB-MS: *m*/*z* 365 $(M + H)^+$. Anal. Calcd for $C_{16}H_{13}O_2I$: C, 52.77; H, 3.60. Found: C, 53.00; H, 3.59.

**2,2′-Bis(3-*p*-tolyl-1,3-dioxopropyl)tolan, $(2\text{-}(p\text{-}CH_3C_6H_4COCH_2\text{-}CO)C_6H_4)C{\equiv}C(2\text{-}C_6H_4COCH_2COC_6H_4\text{-}p\text{-}CH_3)$ ($\mathbf{L}^2H_2$).** In the drybox, 1-(2-iodophenyl)-3-*p*-tolylpropane-1,3-dione (1.192 g, 3.27 mmol), $(Ph_3P)_2PdCl_2$ (Aldrich, 0.138 g, 0.20 mmol), 30 mL of $C_6H_6$, and a magnetic stirbar were placed into a 100 mL round-bottom flask. The flask was capped with a rubber septum and taken out of the drybox. 1,2-Bis(tributylstannyl)ethyne (Aldrich, 0.86 mL, 1.63 mmol) was added to the flask by syringe, and the reaction mixture was heated in an oil bath at 75 °C for 5 h. The dark orange solution was cooled to room temperature and poured into a separatory funnel with 50 mL of saturated aqueous NaF and 20 mL of ether. The yellow organic layer was separated, washed with 50 mL of $H_2O$ and then 50 mL of brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure, leaving a dark orange residue. The residue was extracted with 3 × 20 mL of hexane; the hexane solutions were combined, and the solvent was removed on a rotary evaporator. This material was dissolved in 20 mL of hexane and purified by column chromatography on silica gel, eluting first with hexane and then with 100:1 hexane/ether. The collected fractions were combined, and the solvent was removed on a rotary evaporator, leaving a pale yellow solid, which was vacuum-dried overnight to give 0.20 g $\mathbf{L}^2H_2$ (25%). $^1$H NMR ($C_6D_6$): $\delta$ 1.96 (s, 6H, tolyl C*$H_3$*), 6.82 (dt, 8, 2 Hz, 2H, biphenyl H-4 or -5), 6.85 (d, 8 Hz, 4H, tolyl 3,5-H), 6.91 (td, 8, 2 Hz, 2H, biphenyl H-4 or -5), 7.41 (s, 2H, COC*H*CO), 7.45 (dd, 9, 2 Hz, 2H, biphenyl H-3 or -6), 7.84 (dd, 8, 2 Hz, 2H, biphenyl H-3 or -6), 7.91 (d, 8 Hz, 4H, tolyl 2,6-H), 17.54 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 21.71 (tolyl *C*$H_3$), 95.14 (*C*≡C), 98.01 (CO*C*HCO), 121.79, 128.23, 129.30, 129.56, 129.90, 131.10, 133.63, 134.56, 138.89, 143.65, 185.53 (*C*O), 186.93 (*C*O). IR ($cm^{-1}$): 2360 (w, $\nu_{C\equiv C}$), 2338 (w, $\nu_{C\equiv C}$), 1608 (m), 1583 (w), 1542 (m), 1489 (m), 1457 (w), 1434 (w), 1387 (w), 1314 (w), 1303 (w), 1267 (w), 1256 (w), 1223 (w), 1208 (w), 1208 (w),1184 (w), 1156 (w), 1121 (w), 1110 (w), 1086 (w), 1037 (w), 1018 (w), 987 (w), 972 (w), 946 (w), 840 (w), 827 (w), 798 (m), 759 (s). FAB-MS: *m*/*z* 499 $(M + H)^+$. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26. Found: C, 81.93; H, 5.14.

**2,2′-Biphenyldiacetonitrile, $(2\text{-}NCCH_2C_6H_4)_2$.** $(2\text{-}NCCH_2C_6H_4)_2$ was prepared in according to a literature procedure.[17] $^1$H NMR ($C_6D_6$): $\delta$ 2.59 (s, 4 H, C*$H_2$*), 6.66 (dd, 8, 1 Hz, 2H, 6-H), 6.91 (td, 8, 1 Hz, 2H, 4- or 5-H), 6.97 (td, 8, 2 Hz, 2H, 4- or 5-H), 7.17 (dd, 8, 1 Hz, 2H, 3-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 22.11 (*C*$H_2$), 117.74 (*C*≡N), 128.68, 128.90, 129.43, 129.71, 130.20, 139.10. IR ($cm^{-1}$): 3064 (m), 3026 (m), 2962 (w), 2933 (w), 2249 (m, $\nu_{C\equiv N}$), 1637 (w), 1599 (w), 1578 (w), 1500 (w), 1478 (s), 1442 (s), 1414 (s), 1319 (w), 1186 (w), 1162 (w), 1115 (w), 1052 (w), 1009 (m), 956 (w), 924 (w), 872 (w), 762 (s), 728 (m). FAB-MS: *m*/*z* 233 $(M + H)^+$. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21. Found: C, 83.00; H, 5.03.

**2,2′-Biphenyldiacetic Acid, $(2\text{-}HOOCCH_2C_6H_4)_2$.** $(2\text{-}HOOC\text{-}CH_2C_6H_4)_2$ was prepared using the procedure of Weitzenböck[18] and was isolated in 84% yield. $^1$H NMR ($C_6D_6$): $\delta$ 3.18 (d, 18 Hz, 2H, C*H*H′), 3.61 (d, 18 Hz, 2H, CH*H*′), 6.96 (dd, 8, 1 Hz, 2H, 6-H), 7.01 (td, 7, 2 Hz, 2H, 4- or 5-H), 7.05 (dd, 8, 2 Hz, 2H, 3-H), 7.11 (td, 8, 2 Hz, 2H, 4- or 5-H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 37.99 (*C*$H_2$), 127.61, 128.29, 130.40, 131.66, 132.50, 141.38, 179.79 (*C*OOH). IR ($cm^{-1}$): 3422 (w, v br, $\nu_{OH}$), 3019 (w), 2915 (w), 1693 (s, C═O), 1650 (s, br), 1481 (w), 1437 (w), 1405 (s), 1333 (w), 1316 (w), 1217 (s), 1116 (w), 1008 (w), 909 (m), 878 (w),

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834 (w), 759 (s), 720 (w). FAB-MS: *m*/*z* 271 (M + H)$^+$. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.03; H, 5.15.

**2,2′-Biphenyldiacetyl Chloride, (2-ClCOCH$_2$C$_6$H$_4$)$_2$.** In the drybox, a magnetic stirbar, 2,2′-biphenyldiacetic acid (1.011 g, 3.74 mmol) and $PCl_5$ (1.641 g, 7.88 mmol, Aldrich) were put into a 100 mL round-bottom flask. A Teflon needle valve was attached to the flask, which was then affixed to a vacuum line, and ∼20 mL of $C_6H_6$ was added to the flask by vacuum transfer. The reaction mixture was stirred for 30 min at room temperature, becoming a clear colorless solution after about 15 min of stirring. The solvent was evaporated on the vacuum line using a warm (40 °C) water bath. The thick colorless liquid left in the flask was heated in vacuo with a hot (100 °C) water bath for at least 1 h to sublime any unreacted $PCl_5$. A colorless thick liquid was left, which solidified to a tan solid (1.13 g, 98%) within about 30 min of cooling to room temperature. $^1$H NMR ($C_6D_6$): $\delta$ 3.45 (d, 18 Hz, 2H, C*H*H′), 3.54 (d, 18 Hz, 2H, CH*H*′), 6.84 (dd, 9, 2 Hz, 2 H, 6-H), 6.96 (m, 6 H, aromatic protons). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 51.11 (*C*H$_2$), 128.75, 129.02, 130.53, 130.90, 131.34, 140.71, 172.16 (*C*=O). IR (cm$^{-1}$): 3064 (w), 3024 (w), 2021 (w), 1798 (s, C=O), 1751 (m), 1599 (w), 1501 (w), 1480 (m), 1440 (m), 1402 (m), 1318 (w), 1198 (w), 1162 (w), 1115 (w), 1100 (w), 1033 (s), 1007 (s), 960 (s), 903 (w), 751 (s), 706 (m). Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94. Found: C, 62.80; H, 3.97.

**2,2′-Bis(5,5-dimethyl-2,4-dioxohexyl)biphenyl, (C$_6$H$_4$CH$_2$CO-CH$_2$CO$^t$Bu)$_2$ ($^t$Bu$_2$BobH$_2$).** In the drybox, LiN(SiMe$_3$)$_2$ (1.173 g, 6.99 mmol) was added to a solution of pinacolone (0.85 mL, 6.80 mmol, Aldrich) in 10 mL of THF. After the solution was stirred for 5 min, it was added dropwise to a solution of 2,2′-biphenyldiacetyl chloride (0.512 g, 1.69 mmol) in 10 mL of THF in a 50 mL round-bottom flask. The reaction mixture turned dark yellow. The flask was capped with a rubber septum, taken out of the drybox, and stirred for 2 h in a 75 °C oil bath. The dark brown reaction solution was removed from the bath, cooled to room temperature, and poured into a separatory funnel with 30 mL of 18% HCl and 10 mL of ether. The yellow organic layer was separated and washed with 50 mL of $H_2O$. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator, leaving a brown residue. The compound was purified as described for **L$^1$**H$_2$ to give a thick colorless oil, which was vacuum-dried overnight. Yield 0.14 g, 19%. $^1$H NMR ($C_6D_6$): $\delta$ 0.98 (s, 18H, $^t$Bu), 3.33 (AB quartet, $\Delta\delta_{AB} = 0.034$ ppm, $J = 15.5$ Hz, 4H, C*HH*′), 5.22 (s, 2H, COC*H*CO), 7.07 (m, 6H, aromatic protons), 7.28 (dd, 7, 1 Hz, 2H, 3-H), 16.41 (br s, 2H, O*H*). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 27.58 (*C*H$_3$), 43.66 (*C*(CH$_3$)$_3$), 96.23 (CO*C*HCO), 127.32, 128.41, 130.83, 131.25, 134.66, 141.73, 194.37 (*C*O), 199.83 (*C*O). IR (cm$^{-1}$): 2967 (s), 2941 (m), 2906 (m), 2871 (m), 1698 (m), 1598 (s, v br), 1479 (s), 1462 (m), 1436 (m), 1394 (w), 1364 (m), 1320 (m), 1277 (m), 1220 (m), 1194 (m), 1138 (m), 1055 (w), 1025 (w), 1008 (w), 947 (m), 891 (m), 834 (w), 786 (m), 756 (s). FAB-MS: *m*/*z* 435 (M + H)$^+$.

**($^t$Bu$_2$Bob)Ti(O$^i$Pr)$_2$.** A 130 mL glass bomb was charged with a mixture of 40 mL of $C_6H_6$, $^t$Bu$_2$BobH$_2$ (0.082 g, 0.19 mmol), Ti(O$^i$Pr)$_4$ (0.169 g, 0.60 mmol, Aldrich), 2-propanol (0.04 mL, 0.5 mmol), and a stirbar. The bomb was closed with a Teflon valve, taken out of the drybox, and heated with stirring in a 75 °C oil bath overnight. The solvent was then removed in vacuo, leaving a thick orange liquid. The bomb was opened, and its contents were vigorously stirred for 5 min in ∼20 mL of hexane mixed with 0.3 mL of $H_2O$. This produces a mixture of a yellow solution and a yellow precipitate, which was filtered through a glass frit. The filtrate was collected in a 50 mL round-bottom flask and stripped down under vacuum, leaving a thick light yellow liquid. The product was dried on a vacuum line for 2 h and then stored in the drybox. Yield: 0.089 g, 79%. $^1$H NMR ($C_6D_6$): $\delta$ 1.11 (s, 18H, $^t$Bu), 1.31 (d, 6 Hz, 6H, CH(C*H*$_3$)(CH′$_3$)), 1.36 (d, 6 Hz, 6H, CH(CH$_3$)(C*H*′$_3$)), 2.92 (d, 14 Hz, 2H, C*H*H′), 3.66 (d, 14 Hz, 2H, CH*H*′), 4.67 (sept, 6 Hz, 2H, C*H*(CH$_3$)$_2$), 4.74 (s, 2H, COC*H*CO), 6.98 (m, 8H, aromatic). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 25.26 (CH(*C*H$_3$)(CH′$_3$)), 25.28 (CH(CH$_3$)(*C*H′$_3$)), 28.04 (C(*C*H$_3$)$_3$), 39.73 (*C*(CH$_3$)$_3$), 46.38 (*C*H$_2$), 77.65 (*C*H(CH$_3$)$_2$), 99.30 (CO*C*HCO), 126.74, 127.91, 129.66, 133.23, 137.11, 140.74, 190.16 (*C*O), 196.40 (*C*O). IR (cm$^{-1}$): 2966 (s), 2928 (m), 2864 (m), 1596 (s), 1576 (s), 1510 (s), 1474 (w), 1451 (w), 1438 (w), 1423 (m), 1387 (s), 1358 (s), 1325 (m), 1297 (w), 1262 (m), 1227 (m), 1206 (w), 1164 (s), 1126 (s), 1050 (w), 986 (s), 948 (w), 901 (m), 875 (w), 851 (m), 814 (w), 776 (m), 754 (m), 720 (w). FAB-MS: *m*/*z* 539 (M − O$^i$Pr)$^+$.

**($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$.** ($^t$Bu$_2$Bob)Ti(O$^i$Pr)$_2$ was generated in situ by heating $^t$Bu$_2$BobH$_2$ (0.0675 g, 0.16 mmol) and Ti(O$^i$Pr)$_4$ (0.0549 g, 0.19 mmol) in 30 mL of benzene overnight at 75 °C in a glass bomb. The bomb was then opened briefly to the air, and 2,6-diisopropylphenol (0.070 mL, 0.37 mmol, Aldrich) was syringed into it. The bomb was resealed and heated in the oil bath for a further 5 h. The very dark orange solution was transferred into a 50 mL round-bottom flask in the air, and the solvent was removed on a rotary evaporator. The remaining dark red liquid was dissolved in 5 mL of hexane and purified by column chromatography on silica gel, eluting first with hexane to remove the excess phenol, then with 100:1 hexane/Et$_2$O to elute the desired product. The fractions containing ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$ were combined, and the solvent was removed on a rotary evaporator leaving a very thick dark red liquid. The air-stable compound crystallized only with difficulty, but crystals could be obtained by repeated evaporation from diethyl ether. Yield 0.103 g (79%). $^1$H NMR ($C_6D_6$): $\delta$ 1.05 (s, 18H, $^t$Bu), 1.23 (d, 7 Hz, 12H, CH(C*H*$_3$)(CH′$_3$)), 1.35 (d, 7 Hz, 12H, CH(CH$_3$)(C*H*′$_3$)), 2.92 (d, 14 Hz, 2H, C*H*H′), 3.59 (d, 14 Hz, 2H, CH*H*′), 4.07 (sept, 7 Hz, 4H, C*H*(CH$_3$)$_2$), 4.73 (s, 2H, COC*H*CO), 6.90 (m, 4H, aromatic), 6.97 (m, 6H, aromatic), 7.13 (d, 8 Hz, 4H, OAr 3- and 5-H). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 23.23 (CH(*C*H$_3$)(C′H$_3$)), 24.57 (CH(CH$_3$)(*C*′H$_3$)), 26.23(C(*C*H$_3$)$_3$), 28.04 (*C*H(CH$_3$)$_2$), 39.73 (*C*(CH$_3$)$_3$), 46.40 (*C*H$_2$), 101.88 (CO*C*HCO), 120.83, 122.66, 127.18, 128.54, 129.84, 133.31, 136.69, 138.87, 141.04, 163.14 (OAr *ipso*), 191.34 (*C*O), 196.41 (*C*O). IR (cm$^{-1}$): 3054 (w), 2958 (s), 2915 (m), 2863 (m), 1589 (s), 1586 (m), 1515 (s), 1463 (w), 1431 (m), 1374 (s), 1356 (s), 1331 (s), 1258 (s), 1205 (s), 1167 (w), 1114 (w), 1099 (w), 1046 (w), 1030 (w), 986 (w), 902 (s), 877 (m), 784 (w), 749 (m), 710 (m). FAB-MS (NPOE matrix): *m*/*z* 657 (M − O-2,6-$^i$Pr$_2$C$_6$H$_3$)$^+$. Anal. Calcd for $C_{52}H_{66}O_6Ti$: C, 74.80; H, 7.97. Found: C, 74.99; H, 7.80.

**2,2′-Bis(4-*p*-tolyl-2,4-dioxobutyl)biphenyl (Tol$_2$BobH$_2$, (C$_6$H$_4$CH$_2$COCH$_2$COC$_6$H$_4$-*p*-CH$_3$)$_2$).** In the drybox, a solution of the lithium enolate of 4′-methylacetophenone was prepared by slow addition of a suspension of LiN(SiMe$_3$)$_2$ (2.582 g, 15.4 mmol) in 20 mL of ether to the neat ketone (2.009 g, 15.0 mmol, Aldrich) in a 125 mL Erlenmeyer flask. Some undissolved LiN(SiMe$_3$)$_2$ was washed with 2 × 20 mL of dry ether, and the washes were added to the reaction mixture. The flask was capped with a rubber septum. A solution of 2,2′-biphenyldiacetyl chloride (1.128 g, 3.67 mmol) in 30 mL of ether was prepared in a 50 mL round-bottom flask capped with a rubber septum. The two solutions were taken out of the drybox, and the 125 mL Erlenmeyer flask with the enolate solution was cooled in an ice bath for 20 min. The solution of the acyl chloride was slowly added to the stirring enolate solution by syringe, forming a light yellow precipitate. Any undissolved acyl chloride was dissolved in fresh dry ether and added to the reaction flask. The reaction mixture was stirred for 5 min in the ice bath;

then the precipitate was suction filtered on a glass frit in the air. The yellow solid in the frit was washed with 3 × 20 mL of ice-cold ether and then transferred into a 125 mL Erlenmeyer flask. The volume of the filtrate was reduced to about 50 mL on a rotary evaporator, and then it was cooled in an ice bath for 10 min to produce a second crop of yellow precipitate, which was filtered, washed with 3 × 10 mL of ice-cold ether, and combined with the rest of the solid. The precipitate was digested by stirring with 50 mL of 18% HCl and 50 mL of ether until it had completely dissolved. The mixture was poured into a separatory funnel, and the bottom water layer discarded. The yellow organic solution was washed with 50 mL of saturated $NaHCO_3$ and dried over $MgSO_4$; then it was filtered, and its volume was reduced on a rotary evaporator to about 10 mL. A small stirbar was added, and about 20 mL of methanol was added dropwise with stirring (until the solution started to get slightly cloudy). Stirring was continued overnight with the flask open to the air, during which time a white precipitate formed. The mixture was cooled in an ice bath for about 10 min and filtered on a glass frit. The pale pink solid was washed with 2 × 10 mL of cold methanol and air-dried for 3 h. The filtrate was collected, stripped to dryness, redissolved in 5 mL ether, and treated with about 10 mL of methanol as described above to yield a second crop of a solid product. The overall yield of $Tol_2BobH_2$ was 1.22 g (66%). $^1H$ NMR ($C_6D_6$): $\delta$ 1.97 (s, 6H, Ar$CH_3$), 3.46 (AB quartet, $\Delta\delta_{AB} = 0.025$ ppm, $J_{AB} = 15$ Hz, 4H), 5.77 (s, 2H, COC*H*CO), 6.86 (d, 8.4 Hz, 4H, Tol 3,5-H), 7.05 (td, 7, 2 Hz, 2H, biphenyl 4- or 5-H), 7.12 (td, 7, 2 Hz, 2H, biphenyl 4- or 5-H), 7.16 (obscured by the solvent, 2H, 3- or 6-H), 7.31 (dd, 7, 1 Hz, 2H, 3- or 6-H), 7.69 (d, 8 Hz, 4H, Tol 2,6-H),16.87 (s, 2H, O*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 21.69 ($CH_3$), 43.95 ($CH_2$), 96.92 (COC*H*CO), 127.45, 127.85, 128.51, 129.83, 130.91, 131.32, 132.90, 134.69, 141.79, 143.27, 183.66 (*C*O), 195.03 (*C*O). IR ($cm^{-1}$): 3063 (w), 3026 (w), 2920 (w), 1610 (s, v br, $\nu_{C=O}$), 1568 (s), 1507 (m), 1477 (m), 1441 (m), 1411 (m), 1300 (w), 1290 (w), 1269 (m), 1184 (m), 1143 (w), 1118 (w), 1074 (w), 1019 (w), 1008 (w), 954 (w), 917 (w), 830 (w), 775 (m), 757 (m), 720 (w). FAB-MS: *m/z* 503 (M + H)$^+$. Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.25; H, 6.02. Found: C, 80.94; H, 5.97.

**$(Tol_2Bob)Ti(O^iPr)_2$.** The alkoxide complex was generated as described for $(^tBu_2Bob)Ti(O^iPr)_2$, using 1.483 g of $Tol_2BobH_2$ (2.95 mmol), 2.204 g of $Ti(O^iPr)_4$ (7.74 mmol), 0.6 mL of 2-propanol (7.8 mmol), and 100 mL of $C_6H_6$. After it was heated overnight in a 75 °C oil bath, the bomb was affixed to a vacuum line, and the solvent was reduced to ~20 mL, at which point a yellow precipitate formed. The bomb was taken into the drybox, and the contents (a dark orange solution and yellow solid) were filtered on a glass frit. The precipitate was washed with 3 × 20 mL of hexane; then the frit with the pale yellow solid was taken out of the drybox and air-dried on a vacuum pump for 30 min. The isolated complex (1.68 g, 85%) was promptly stored in the drybox. $^1H$ NMR ($C_6D_6$): $\delta$ 1.41 (d, 6 Hz, 6H, $CH(CH_3)(CH'_3)$), 1.48 (d, 6 Hz, 6H, $CH(CH_3)(CH'_3)$), 2.08 (s, 6H, tolyl $CH_3$), 2.99 (d, 14 Hz, 2H, C*H*H′), 3.76 (d, 14 Hz, 2H, CH*H′*), 5.20 (sept, 6 Hz, 2H, $CH(CH_3)_2$), 5.34 (s, 2H, C*H*), 6.88 (m, 4H, biphenyl H-5,6), 6.99 (d, 8 Hz, 4H, Tol 3,5-H), 7.05 (m, 4H, biphenyl H-3,4), 7.88 (d, 8 Hz, 4H, Tol 2,6-H). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 21.74 (tolyl $CH_3$), 26.18 ($CH(CH_3)_2$) [the diastereotopic carbons are accidentally degenerate], 46.92 ($CH_2$), 78.97 ($CH(CH_3)_2$), 100.99 (COC*H*CO), 127.12, 128.71, 129.50, 129.97, 133.88, 135.39, 137.66, 141.21, 142.25, 180.60 (*C*-O), 191.01 (*C*-O); one aromatic carbon resonance is obscured by the solvent peak. IR ($cm^{-1}$): 3063 (w), 3023 (w), 2967 (w), 2923 (w), 2861 (w), 1598 (s), 1581 (m), 1557 (m), 1519 (s), 1497 (s), 1413 (m), 1372 (s), 1322 (m), 1299 (w), 1184 (m), 1154 (m), 1120 (m), 983 (m), 850 (w), 811 (w), 794 (w), 771 (m), 751 (w), 722 (w). FAB-MS (NPOE matrix): *m/z* 607 $(M - O^iPr)^+$. Anal. Calcd for $C_{40}H_{42}O_6Ti$: C, 72.07; H, 6.35. Found: C, 72.08; H, 6.25.

**$(Tol_2Bob)Ti(O^iPr)(OSO_2CF_3)$.** In the drybox, trimethylsilyl trifluoromethanesulfonate (0.42 mL, 2.10 mmol, Aldrich) was added dropwise into a vigorously stirred solution of $(Tol_2Bob)Ti(O^iPr)_2$ (1.412 g, 2.12 mmol) in 30 mL of $C_6H_6$. The solution turned orange immediately, and an orange precipitate formed. After the mixture was stirred for 1 h at room temperature, the solid was filtered on a glass frit, washed with 3 × 20 mL of hexane, and vacuum-dried for 5 h, giving 1.33 g (83%) of yellow-orange $(Tol_2Bob)Ti(O^iPr)(OSO_2CF_3)$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 1.36 (d, 6 Hz, 6H, $CH(CH_3)_2$), 2.43 (s, 3H, tolyl $CH_3$), 2.44 (s, 3H, tolyl $CH_3$), 3.23 (d, 14 Hz, 1H, C*H*H′), 3.25 (d, 14 Hz, 1H, C*H*H′), 4.03 (d, 14 Hz, 1H, CH*H′*), 4.09 (d, 14 Hz, 1H, CH*H′*), 5.09 (sept, 6 Hz, 1H, $CH(CH_3)_2$), 5.55 (s, 1H, COC*H*CO), 5.59 (s, 1H, COC*H*CO), 7.10 (m, 4H, biphenyl Ar*H*), 7.27 (d, 8 Hz, 2H, tolyl 3,5-H), 7.28 (d, 8 Hz, 2H, tolyl 3,5-H), 7.38 (m, 2H, biphenyl Ar*H*), 7.45 (td, 6, 2 Hz, 1H, biphenyl H-4 or 5), 7.48 (td, 6, 2 Hz, 1H, biphenyl H-4 or 5), 7.65 (d, 8 Hz, 2H, tolyl 2,6-H), 7.72 (d, 8 Hz, 2H, tolyl 2,6-H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 21.99 (tolyl $CH_3$), 22.13 (tolyl $CH_3$), 24.62 ($CH(CH_3)(C'H_3)$), 24.70 ($CH(CH_3)(C'H_3)$), 45.29 ($CH_2$), 46.56 ($CH_2$), 86.60 ($CH(CH_3)_2$), 103.69 (CO*C*HCO), 104.56 (CO*C*HCO), 120.15 (q, 319 Hz, $CF_3$), 127.77, 128.08, 128.42, 128.96, 129.13, 129.47, 129.81, 129.91, 130.02, 130.43, 131.64, 132.42, 133.46, 133.73, 135.67, 136.84, 140.54, 140.97, 144.33, 145.82, 179.88 (*C*O), 184.86 (*C*O), 189.44 (*C*O), 193.88 (*C*O). $^{19}F$ NMR ($CD_2Cl_2$): $\delta$ −77.83. IR (Nujol mull, $cm^{-1}$): 1610 (w), 1589 (w), 1519 (m), 1501 (m), 1363 (m), 1358 (m, $\nu_{SO_3}$), 1338 (m), 1319 (w),1300 (w), 1284 (w), 1236 (w), 1202 (s, $\nu_{CF_3}$), 1184 (m), 1156 (w), 1123 (w), 1116 (w), 1003 (w), 983 (w), 866 (w), 831 (w), 793 (w), 770 (w), 746 (w). Anal. Calcd for $C_{38}H_{35}F_3O_8STi$: C, 60.32; H, 4.66. Found: C 57.93; H, 4.69.

**$(Tol_2Bob)Ti(OSO_2CF_3)_2$.** A sample of $(Tol_2Bob)Ti(O^iPr)_2$ (0.52 g, 0.78 mmol) was dissolved in 10 mL of $CHCl_3$ in the drybox. The yellow solution was stirred vigorously, while trifluoromethanesulfonic acid (0.20 mL, 2.26 mmol) was added dropwise to it. The solution immediately turned dark red-brown, and a dark red precipitate formed. After 30 min, 30 mL of hexane was added to the reaction mixture, and the solid was filtered on a glass frit and washed with 3 × 20 mL of hexane. To remove any excess triflic acid, the moist solid product was transferred into a 50 mL Erlenmeyer flask, where it was stirred with 20 mL of ether for 10 min at room temperature and then cooled at −40 °C for 30 min. The dark red solid was filtered on a glass frit, washed with 3 × 20 mL of cold ether and vacuum-dried for 5 h, yielding 0.48 g (73%) of the bis(triflate) complex. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.47 (s, 6H, tolyl $CH_3$), 3.37 (d, 14 Hz, 2H, C*H*H′), 4.19 (d, 14 Hz, 2H, CH*H′*), 5.92 (s, 2H, COC*H*CO), 7.15 (m, 4H, biphenyl Ar*H*), 7.35 (d, 8 Hz, 4H, Tol 3,5-H), 7.45 (d, 7 Hz, 2H, biphenyl H-3 or 6), 7.52 (m, 2H, biphenyl Ar*H*), 7.77 (d, 8 Hz, 4H, Tol 2,6-H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 22.45 (tolyl $CH_3$), 44.76 ($CH_2$), 108.79 (CO*C*HCO), 128.65, 128.90, 129.65, 130.20, 130.36, 130.72, 133.79, 135.38, 140.52, 148.84, 185.50 (*C*O), 190.93 (*C*O); $CF_3$ not observed. $^{19}F$ NMR ($CD_2Cl_2$): $\delta$ −77.28. IR (Nujol mull, $cm^{-1}$): 1607 (w), 1538 (s), 1507 (s), 1485 (m), 1420 (w), 1364 (s), 1347 (s, $\nu_{SO_3}$), 1321 (w), 1303 (w), 1286 (w), 1267 (w), 1242 (w), 1190 (s), 1151 (m), 1125 (w), 1112 (w), 1094 (w), 1003 (m), 965 (s), 866 (w), 832 (w), 799 (w), 770 (w), 760 (w), 748 (w), 737 (w). Anal. Calcd for $C_{38}H_{35}F_6O_{10}S_2Ti$: C, 51.07; H, 3.33. Found: C, 51.41; H, 3.36.

**$(Tol_2Bob)TiCl_2$.** On the benchtop, a magnetic stirbar, $(Tol_2Bob)Ti(O^iPr)_2$ (0.22 g, 0.33 mmol), and 10 mL of $CH_2Cl_2$ were put into a 25 mL round-bottom flask. The flask was placed on a stirring plate, and chlorotrimethylsilane (1.0 mL, 7.9 mmol) was added dropwise to the vigorously stirred yellow solution. The solution turned red, and a red precipitate formed. After 30 min at room temperature, the mixture was stirred for 20 min while being cooled in an ice bath. The solid was filtered on a glass frit, washed with 3 × 20 mL of cold $CH_2Cl_2$, and air-dried overnight to give 0.17 g (82%) of the dichloride complex. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.45 (s, 6H, Tol C$H_3$), 3.30 (d, 14 Hz, 2H, C*H*H′), 4.10 (d, 14 Hz, 2H, CH*H*′), 5.68 (s, 2H, COC*H*CO), 7.09 (m, 4H, biphenyl Ar*H*), 7.30 (d, 8 Hz, 4H, Tol 3,5-H), 7.39 (d, 7 Hz, 2H, biphenyl H-3 or -6), 7.48 (td, 8, 2 Hz, 2H, biphenyl H-4 or -5), 7.69 (d, 8 Hz, 4H, Tol 2,6-H). The compound was insufficiently soluble for $^{13}C\{^1H\}$ NMR analysis. IR (cm$^{-1}$): 1558 (m), 1550 (m), 1541 (m), 1527 (w), 1514 (m), 1508 (s), 1498 (s), 1474 (w), 1462 (w), 1457 (w), 1431 (m), 1340 (w), 1326 (m), 1296 (m), 1185 (m), 1158 (m), 1122 (w), 1097 (w), 1061 (w), 1012 (w), 976 (m), 850 (w), 831 (w), 795 (w), 771 (w), 755 (w). FAB-MS (NPOE matrix): $m/z$ 583 $(M - Cl)^+$. Anal. Calcd for $C_{34}H_{28}O_4Cl_2Ti$: C, 65.93; H, 4.56. Found: C, 65.81; H, 4.59.

**[(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$.** In the drybox, a magnetic stirbar, (Tol$_2$Bob)Ti(O$^i$Pr)(OSO$_2$CF$_3$) (0.206 g, 0.27 mmol), NaBAr$_F$ (0.242 g, 0.27 mmol), and 20 mL of $CH_2Cl_2$ were put into a 50 mL round-bottom flask. The flask was placed on a stirring plate, and the yellow-brown slurry was stirred for 5 min at room temperature. The mixture was filtered through a glass frit, and the filtrate was collected into a 50 mL round-bottom flask. A Teflon needle valve was attached to the flask, which was then affixed to the vacuum line. The solvent was completely removed, leaving a dark red residue. The flask was taken back into the drybox, and the crude product was dissolved in a minimum amount of ether (~5 mL). Hexane (30 mL) was added to the stirred orange solution, which led to the formation of an orange precipitate. This slurry was vigorously stirred for 30 min, filtered through a glass frit, and the solid was washed with 3 × 10 mL of hexane. After it was washed, the yellow solid was vacuum-dried overnight, yielding 0.321 g (76%) of [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$. $^1$H NMR ($CD_2Cl_2$, 500 MHz, −15 °C): $\delta$ 1.24 (t, 7 Hz, 6H, Ti[O(CH$_2$C$H_3$)$_2$]), 1.31 (d, 6 Hz, 3H, CH(C$H_3$)(CH′$_3$)), 1.35 (d, 6 Hz, 3H, CH(CH$_3$)(C$H'_3$)), 2.40 (s, 3H, tolyl C$H_3$), 2.41 (s, 3H, tolyl C$H_3$), 3.12 (d, 14 Hz, 1H, C*H*H′), 3.24 (d, 14 Hz, 1H, C*H*H′), 4.11 (m, 6H, 2 CH*H*′ + Ti[O(C$H_2$CH$_3$)$_2$]), 5.00 (sept, 6 Hz, 1H, C*H*(CH$_3$)$_2$), 5.61 (s, 1H, COC*H*CO), 5.69 (s, 1H, COC*H*CO), 7.03 (d, 7 Hz, 1H, biphenyl H-6), 7.09 (pseudo-*d*, $J_{app} = 4$ Hz, 2H, biphenyl H-5′,-6′), 7.17 (td, 7, 2 Hz, 1H, biphenyl H-5), 7.28 (d, 8 Hz, 2H, Tol 3,5-H), 7.29 (d, 9 Hz, 2H, Tol 3,5-H), 7.40 (d, 7 Hz, 1H, biphenyl H-3′), 7.42 (d, 8 Hz, 1H, biphenyl H-3), 7.48 (m, 1H, biphenyl H-4′), 7.53 (s, 4H, BAr$_F$ H-4), 7.55 (td, 8, 1 Hz, 1H, biphenyl H-4), 7.58 (d, 9 Hz, 2H, Tol 2,6-H), 7.63 (d, 9 Hz, 2H, Tol 2,6-H), 7.71 (s, 8H, BAr$_F$ 2,6-H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 500 MHz, −15 °C): $\delta$ 13.29 (Ti[O(CH$_2$*C*H$_3$)$_2$]), 21.92 (Tol *C*H$_3$), 22.00 (Tol *C*H$_3$), 24.57 (CH(*C*H$_3$)(C′H$_3$)), 24.67 (CH(CH$_3$)(*C*′H$_3$)), 44.73 (Bob *C*H$_2$), 46.51 (Bob *C*H$_2$), 70.02 (Ti[O(*C*H$_2$CH$_3$)$_2$]), 87.29 (*C*H(CH$_3$)$_2$), 104.12 (CO*C*HCO), 105.02, (CO*C*HCO), 117.75, 124.76 (q, 272 Hz, *C*F$_3$), 128.17, 128.27, 128.58, 128.86, 128.95, 129.10, 129.20, 129.33, 129.74, 130.04, 130.13, 130.37, 130.60, 133.17, 134.86, 134.97, 134.97, 135.86, 140.09, 140.27, 145.72, 146.77, 161.95 (1:1:1:1 q, $J^{11}_{B-C} = 50$ Hz, BAr$_F$ *ipso*), 180.52 (*C*O), 184.87 (*C*O), 190.14 (*C*O), 193.95 (*C*O). $^{19}$F NMR ($CD_2Cl_2$): $\delta$ −114.49. IR (Nujol mull, cm$^{-1}$): 1610 (w), 1585 (w), 1551 (m), 1514 (s), 1498 (s), 1420 (w), 1354 (s), 1333 (m), 1319 (m), 1274 (s), 1184 (m), 1160 (s), 1136 (s), 1115 (s), 1016 (m), 987 (m), 977 (m), 951 (w), 928 (w), 884 (m), 865 (w), 838 (w), 788 (m), 770 (w), 757 (w). Anal. Calcd for $C_{73}H_{57}BF_{24}O_6Ti$: C, 56.76; H, 3.72. Found: C, 56.22; H, 3.63.

**Table 1.** Crystal Data for ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O and [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$

| | ($^t$Bu$_2$Bob)Ti (O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O | [(Tol$_2$Bob)Ti (O$^i$Pr)(OEt$_2$)]BAr$_F$ |
|---|---|---|
| empirical formula | $C_{56}H_{76}O_7Ti$ | $C_{73}H_{57}BF_{24}O_6Ti$ |
| temp (K) | 100(2) | 100(2) |
| $\lambda$(Mo K$\alpha$) (Å) | 0.71073 | 0.71073 |
| space group | *Pbcn* | $P2_1/c$ |
| total data collected | 97 919 | 119 625 |
| independent reflns | 6400 | 17 228 |
| $R_{int}$ | 0.0642 | 0.0287 |
| obsd reflns [$I > 2\sigma(I)$] | 5380 | 13 862 |
| $a$ (Å) | 12.1602(8) | 19.8094(8) |
| $b$ (Å) | 24.5344(15) | 20.0119(8) |
| $c$ (Å) | 16.4754(11) | 18.8586(7) |
| $\alpha$ (deg) | 90 | 90 |
| $\beta$ (deg) | 90 | 113.367(2) |
| $\gamma$ (deg) | 90 | 90 |
| $V$ (Å$^3$) | 4915.3(6) | 6862.8(5) |
| $Z$ | 4 | 4 |
| cryst size (mm) | 0.49 × 0.44 × 0.15 | 0.49 × 0.47 × 0.35 |
| refined params | 444 | 1184 |
| R indices [$I > 2\sigma(I)$]$^a$ | R1 = 0.0458, wR2 = 0.1213 | R1 = 0.0464, wR2 = 0.1171 |
| R indices (all data)$^a$ | R1 = 0.0573, wR2 = 0.1309 | R1 = 0.0621, wR2 = 0.1326 |
| GOF | 1.085 | 1.034 |

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

**X-ray Crystallography of ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O and [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$.** Crystals of ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$, as the diethyl etherate, were grown by cooling an ether solution of the complex to −40 °C. Crystals of [(Tol$_2$Bob)-Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$ were grown by layering a solution of the complex in ether with hexane. The crystals were 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, with remaining nonhydrogen atoms found on difference Fourier maps. All heavy atoms were refined anisotropically. The titanium complex in ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O lies on a crystallographic 2-fold axis. The ether of crystallization also lies along a crystallographic 2-fold axis and is disordered; it was modeled in two symmetry-related orientations at half occupancy, except that two distinct sites for the oxygen atom, summing to half occupancy, were included in the model. One of the CF$_3$ groups in [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$ was slightly disordered and was refined in two different orientations, with the major orientation refining to 88.9(3)% occupancy. All hydrogen atoms, except those on the disordered ether, were located on difference maps and refined isotropically. Calculations used SHELXTL (Bruker AXS) with scattering factors and anomalous dispersion terms taken from the literature.[19] Further details about the individual structures are given in Table 1.

## Results and Discussion

**Preparation and Metalation of Bis($\beta$-Diketonates).** $\beta$-Diketones are classically prepared by Claisen condensa-

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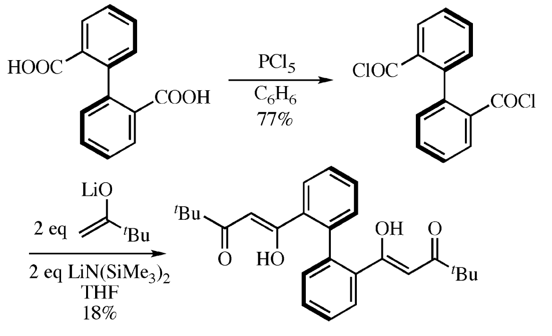
[19] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol C.

**Scheme 1.** Preparation of Biphenyl-Bridged Bis($\beta$-diketone) $\mathbf{L^1}H_2$

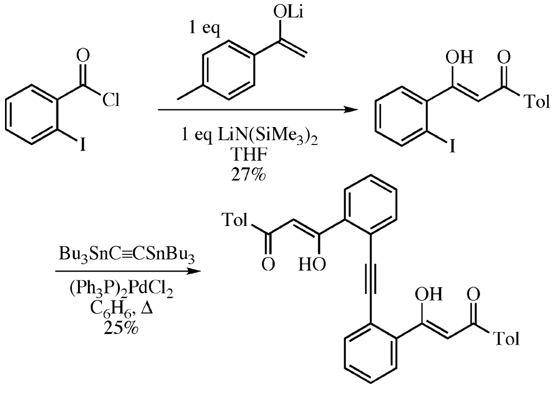


$\mathbf{L^1}H_2$

tion,[20] and we have found Claisen condensation between lithium enolates and acyl chlorides (in the presence of excess base, to neutralize the acidic $\beta$-hydrogen generated by the condensation) to be effective in the synthesis of both unhindered[21] and sterically hindered[9] diketonates. This method works for the preparation of 2,2′-bis(4,4-dimethyl-1,3-dioxopentyl)biphenyl ($\mathbf{L^1}H_2$, Scheme 1), although difficulties in purification lead to a low yield. Biphenyl bridges have been used successfully to create mononuclear complexes; for example, Scott and co-workers have used 6,6′-dimethyl-2,2′-biphenyldiamine as the core of bis(salicylaldimine) ligands that chelate well to titanium(IV) and zirconium(IV).[22] Analogous binaphthyl bridges have also been used in bis(salicylaldimine)[23] or bis(8-hydroxyquinoline)[24] ligands. However, the structural features of the diketonate moiety, in particular the way that the sites of attachment point away from the metal center, suggested that the biphenyl bridge might be too small to allow chelation of both diketonates to the same metal center. Inspection of molecular models confirmed that chelation of $\mathbf{L^1}$ to a single titanium would engender substantial strain.

Indeed, attempted metalation of $\mathbf{L^1}H_2$ with $Ti(O^iPr)_4$ does not result in high yields of a monomeric product. Examination of the reaction mixture in situ by $^1H$ NMR indicates the immediate loss of 2 equiv of free 2-propanol, consistent with metalation, but the spectrum consists principally of broad resonances at the chemical shifts expected for the *tert*-butyl, isopropyl, diketonate methine, and aromatic resonances. The broadness of the resonances suggests that metalation forms a mixture of oligomers $\{\mathbf{L^1}Ti(O^iPr)_2\}_n$, where the two diketonate moieties in any given ligand are bound to two different titanium centers. The $^1H$ NMR spectrum does show some sharp resonances (~10% of the total integral) indicative of a discrete species with $C_2$ symmetry of stoichiometry $\mathbf{L^1}Ti(O^iPr)_2$, as indicated for example, by the observation of diastereotopic isopropoxide methyl groups and a single isopropoxide methine resonance. This complex is tentatively assigned as a monomer, but detailed characterization is precluded by its low yield and its rapid decomposition (the sharp NMR signals disappear within 5 h at room temperature).

**Scheme 2.** Preparation of Tolan-Bridged Bis($\beta$-diketone) $\mathbf{L^2}H_2$



$\mathbf{L^2}H_2$

Given the apparent thermodynamic instability of any monomeric complex of $\mathbf{L^1}$, it seemed likely that a larger linker would be needed to favor binding of both ends of a bis(diketonate) to titanium(IV). Molecular models suggested that the addition of a two-carbon linker ($CH_2CH_2$, *trans*-CH═CH, or C≡C) between the two phenyl rings of $\mathbf{L^1}H_2$ would result in an unstrained monomeric titanium complex. Preparation of the tolan-bridged ligand $\mathbf{L^2}H_2$ (Scheme 2) was achieved through initial formation of an unsymmetrical dibenzoylmethane containing a 2-iodo substituent. The alkyne was then installed by Stille coupling using commercially available 1,2-bis(tributylstannyl)acetylene.

The crude mixture resulting from reaction of $\mathbf{L^2}H_2$ with $Ti(O^iPr)_4$ contains principally (~85% of the total $^1H$ NMR signal) two discrete species with the stoichiometry $\mathbf{L^2}Ti(O^iPr)_2$, a $C_2$-symmetric complex and a $C_1$-symmetric complex formed in a ~1:2 ratio. The invariance of this ratio with time suggests that it represents a thermodynamic distribution and therefore that the species interconvert relatively readily; this is confirmed by the broadening and coalescence of the resonances in the NMR at higher temperatures. As in other octahedral complexes of linear tetradentate ligands,[25] monomeric $\mathbf{L^2}Ti(O^iPr)_2$ could exist in three possible geometric isomers, one isomer where the isopropoxides would be trans and two where they would be cis, a cis-α isomer in which the two tolyl-substituted carbonyls would be trans to each other and a cis-$\beta$ isomer in which these two carbonyls would be cis. The observed symmetries are consistent with the $C_2$-symmetric species being the monomeric cis-α complex and the $C_1$-symmetric species being the cis-$\beta$ complex (eq 2). The remaining ~15% of material consists of several sets of

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(20) Hauser, C. R.; Swamer, F. W.; Adams, J. T. *Org. React.* **1954**, *8*, 59−196.

(21) Fortner, K. C.; Bigi, J. P.; Brown, S. N. *Inorg. Chem.* **2005**, *44*, 2803−2814.

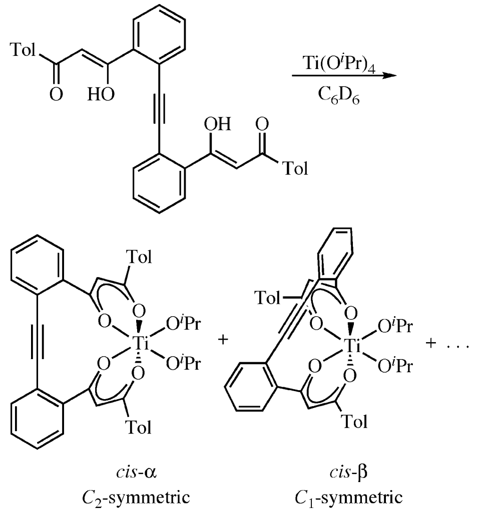
(22) (a) Woodman, P. R.; Munslow, I. J.; Hitchcock, P. B.; Scott, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4069−4076. (b) Woodman, P. R.; Alcock, N. W.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3340−3346. (c) Knight, P. D.; O'Shaughnessy, P. N.; Munslow, I. J.; Kimberley, B. S.; Scott, P. *J. Organomet. Chem.* **2003**, *683*, 103−113.

(23) (a) Cheng, M.-C.; Chan, M. C.-W.; Peng, S.-M.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1997**, 3479−3482. (b) Zhou, X.-G.; Huang, J.-S.; Ko, P.-H.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1999**, 3303−3309. (c) Evans, D. A.; Janey, J. M.; Magomedov, N.; Tedrow, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1884−1888.

(24) Takenaka, N.; Xia, G.; Yamamoto, H. *J. Am. Chem. Soc.* **2004**, *126*, 13198−13199.

(25) Knight, P. D.; Scott, P. *Coord. Chem. Rev.* **2003**, *242*, 125−143.

signals, possibly indicating that some small oligomers are also formed.



*cis*-α $C_2$-symmetric

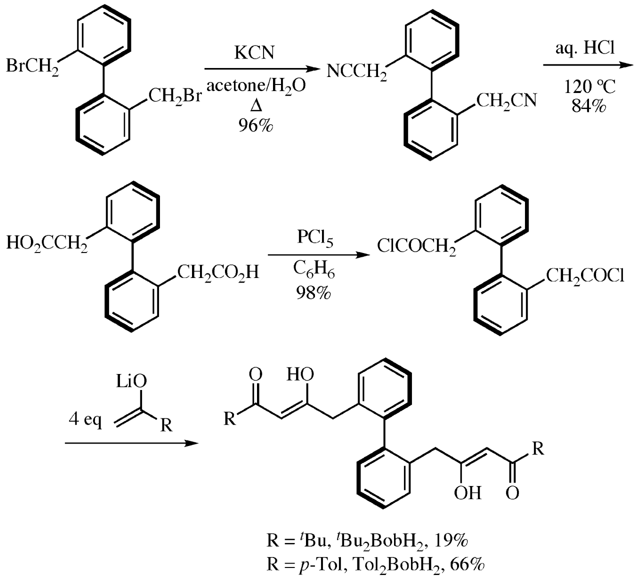
*cis*-β $C_1$-symmetric

(2)

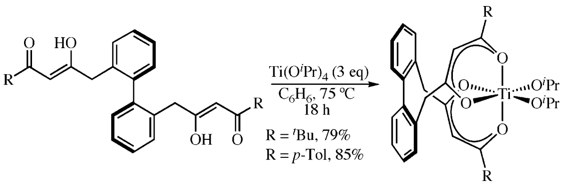
These results suggested that an ideal mononucleating bis($\beta$-diketonate) would need a linker that would exert less strain than the biphenyl bridge in $\mathbf{L^1}$, to permit a thermodynamically stable chelate, but would be significantly more constraining than the tolan bridge in $\mathbf{L^2}$, to avoid formation of multiple isomers. Inspection of molecular models indicated that the addition of the two carbons on the *outside* of the biphenyl moiety in $\mathbf{L^1}$, to give a 2,2′-bis(methylene)biphenyl linker, would have exactly this effect. This linker appeared (unsurprisingly) to be less strained in the metal complex than the smaller biphenyl linker, but it appeared to exert a much tighter fit than the tolan (or stilbene or bibenzyl) bridge, despite forming a ring of the same nominal size.

Preparation of the 2,2′-bis(2,4-dioxobutyl)biphenyl derivatives $R_2BobH_2$ (Scheme 3) proceeds from commercially available 2,2′-bis(bromomethyl)biphenyl via known biphenyldiacetonitrile[17] and -diacetic acid,[18] which is then converted to the acyl chloride with phosphorus pentachloride. In this case, treatment of the diacyl chloride with 2 equiv of enolate and 2 equiv of lithium hexamethyldisilazide fails, presumably because the excess base reacts with the α-protons of the acid chloride. Instead, two additional equivalents of enolate must be used as the base to react with the acidic protons of the $\beta$-diketone after initial acylation of the enolate. This regenerates 2 equiv of the ketone as a side product. For the *tert*-butyl derivative, $^t\mathrm{Bu}_2\mathrm{BobH}_2$, the pinacolone can be evaporated (although difficulties in purification of the oily diketone lead to low isolated yields), but removal of the 4′-methylacetophenone from the bis(diketone) $Tol_2BobH_2$ proved to be more problematic. The compounds did not separate well upon chromatography on silica gel, and attempted removal of the acetophenone by vacuum distillation resulted in thermal decomposition of the bis(diketone). However, the initially formed lithium bis(diketonate) precipitated readily from ether and could be filtered away from the soluble ketone, giving the pure $Tol_2BobH_2$ ligand after acidification of the lithium derivative.

**Scheme 3.** Preparation of 2,2′-Bis(methylene)biphenyl-Linked Bis($\beta$-diketones), $R_2BobH_2$



Metalation of the $R_2BobH_2$ ligands proceeds rapidly at room temperature in benzene to give about a 50% yield of monomeric $(R_2Bob)Ti(O^iPr)_2$ and about 50% of oligomers, as judged by the broad resonances in the $^1$H NMR spectra of the crude reaction mixtures. This mixture is kinetically quite stable, but heating overnight at 75 °C in the presence of excess $Ti(O^iPr)_4$ results in conversion of the mixture to the monomeric compound (eq 3). The yield of monomer is quantitative by NMR, although there are losses upon isolation. Titanium isopropoxide is necessary to catalyze this redistribution reaction because the mixture is not completely equilibrated even upon heating for 4 d at 75 °C in the absence of excess titanium alkoxide. Excess 2-propanol can also be added to the reaction mixture, but it appears to have little effect on the rate of redistribution. The diketonate complex can be freed from excess $Ti(O^iPr)_4$ either by selective hydrolysis of the latter or (in the case of the less soluble tolyl derivative) by precipitation of the $(Tol_2Bob)Ti(O^iPr)_2$.



(3)

**Structure and Spectroscopy of $(R_2Bob)Ti(OR')_2$ Complexes.** The isolated $(R_2Bob)Ti(O^iPr)_2$ complexes appear to be monomeric, as judged by mass spectrometry, where the FAB mass spectra show strong peaks from $[(R_2Bob)Ti(O^iPr)]^+$. NMR spectroscopy of the complexes is consistent with their adopting a single geometric isomer of $C_2$ symmetry, with diastereotopic methyl groups of the isopropoxides and very well-separated resonances for the diastereotopic methylene protons of the bis(methylene)biphenyl linker (e.g., $\Delta\delta = 1.77$ ppm for $(Tol_2Bob)Ti(O^iPr)_2$ in $C_6D_6$). In the free ligand, the methylene protons are also diastereotopic because racemization of the biphenyl is slow on the NMR time scale,

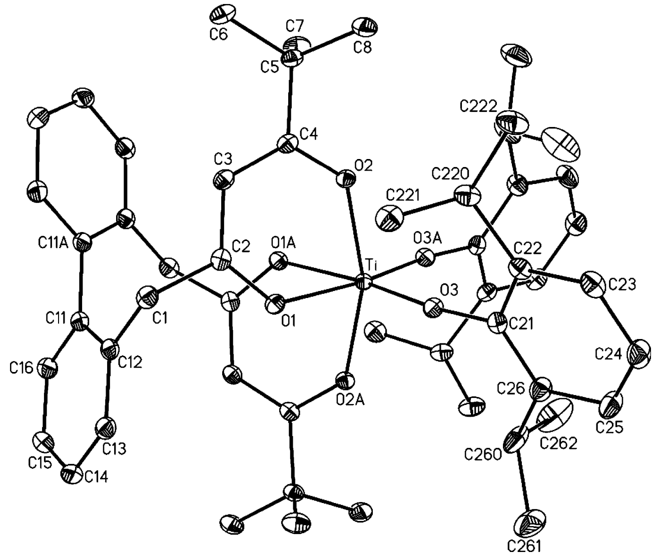


**Figure 1.** Thermal ellipsoid plot (40% ellipsoids) of ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O, with hydrogen atoms and solvent of crystallization omitted for clarity.

as expected for ortho substituents of this size,[26] but the difference in chemical shift between the two protons is very small (<0.03 ppm in C$_6$D$_6$). This suggests that the conformation of the bound ligand is quite different from that of the free ligand. Further evidence of an unusual conformation when bound is the substantial *upfield* shift of the α proton of the bound diketonate compared to that of the enol form of the free ligand ($\Delta\delta = -0.48$ and $-0.43$ ppm, respectively, for $^t$Bu$_2$- and Tol$_2$BobH$_2$ upon coordination to form the Ti(O$^i$Pr)$_2$ complex). This contrasts with the small and generally downfield shifts upon formation of titanium complexes of typical diketones[13b] and suggests that the bound R$_2$Bob ligand may place the α proton in the shielding cone of the biphenyl backbone.

Details of the structure are supplied by crystallography of the bis(2,6-diisopropylphenoxide) complex ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$, obtained from the diisopropoxide by treatment with the phenol (Figure 1, Table 1). The molecule lies on a crystallographic 2-fold axis. The bis(methylene)biphenyl linker completes an eleven-membered chelate ring connecting the two diketonates to each other, and this ring includes two transoid linkages (Ti−O1−C2−C1 and its symmetry-equivalent dihedral angle = 163.7°). The biphenyl moiety is twisted with a dihedral angle of 109.8°.

The bond distances and angles (Table 2) are strikingly similar to those of unconstrained (acac)$_2$Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$.[27] The most significant variation, the (presumably correlated) shortening of the titanium−aryloxide distance by ~0.02 Å and the lengthening of the *trans*-titanium−diketonate distance by ~0.03 Å in the $^t$Bu$_2$Bob complex compared to the acac complex, might plausibly be attributed to tension in the chelate ring serving to pull O1 and O1A away from the titanium. The smaller O1−Ti−O1A angle (79.99(6)° compared to 83.1(2)° in the acac derivative) would support this interpretation. But these distortions are rather modest and do not even fall outside the normal range of variation in unconstrained titanium diketonates. For example, the oxo cluster [(dbm)$_2$Ti]$_3$(Cp*Ti)$_2$($\mu$-O)$_6$ has Ti−O distances (trans to oxo) ranging from 2.092 to 2.126 Å and angles of 79.0−80.1°.[28]

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O and (acac)$_2$Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$

| | ($^t$Bu$_2$Bob)Ti (O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$·Et$_2$O | (acac)$_2$Ti (O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$[a] |
|---|---|---|
| Ti−O1 | 2.0808(11) | 2.046(5) |
| Ti−O2 | 1.9685(10) | 1.985(5) |
| Ti−O3 | 1.8173(11) | 1.834(5) |
| O1−C2 | 1.2685(18) | 1.28(1) |
| C2−C3 | 1.407(2) | 1.41(1) |
| C3−C4 | 1.385(2) | 1.38(1) |
| C4−O2 | 1.2922(18) | 1.28(1) |
| O3−C21 | 1.3555(18) | 1.34(1) |
| O1−Ti−O1A | 79.99(6) | 83.1(2) |
| O1−Ti−O2 | 82.62(4) | 82.8(2) |
| O1−Ti−O2A | 82.60(4) | 83.5(2) |
| O1−Ti−O3 | 91.39(5) | 89.9(2) |
| O1−Ti−O3A | 171.18(5) | 172.1(2) |
| O2−Ti−O2A | 160.67(6) | 161.7(3) |
| O2−Ti−O3 | 98.28(4) | 99.2(2) |
| O2−Ti−O3A | 94.46(5) | 92.9(2) |
| O3−Ti−O3A | 97.28(7) | 97.3(2) |
| Ti−O3−C21 | 170.25(10) | 162.2(4) |

[a] Data from ref 27.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$

| | |
|---|---|
| Ti−O1 | 1.9438(15) |
| Ti−O2 | 1.9482(14) |
| Ti−O3 | 2.0185(13) |
| Ti−O4 | 1.9645(13) |
| Ti−O5 | 1.7488(13) |
| Ti−O6 | 2.0878(14) |
| O1−Ti−O2 | 85.70(6) |
| O1−Ti−O3 | 83.15(6) |
| O1−Ti−O4 | 95.87(6) |
| O1−Ti−O5 | 95.10(6) |
| O1−Ti−O6 | 167.37(5) |
| O2−Ti−O3 | 84.21(5) |
| O2−Ti−O4 | 167.02(6) |
| O2−Ti−O5 | 101.04(6) |
| O2−Ti−O6 | 86.09(5) |
| O3−Ti−O4 | 83.18(5) |
| O3−Ti−O5 | 174.35(6) |
| O3−Ti−O6 | 86.49(5) |
| O4−Ti−O5 | 91.68(6) |
| O4−Ti−O6 | 90.04(5) |
| O5−Ti−O6 | 95.88(6) |
| Ti−O5−C01 | 157.45(13) |
| Ti−O6−C05 | 121.41(11) |
| Ti−O6−C06 | 124.76(11) |
| C05−O6−C06 | 113.80(15) |

The R$_2$Bob framework appears to have remarkably strong preferences in its coordination geometry. Only the cis-α geometry is observed, in contrast to **L**$^2$ and the chelating diketonate−phenoxide that we prepared earlier, which showed little discrimination between fac and mer geometries.[9] The geometric preferences of biphenyl- or binaphthyl-bridged

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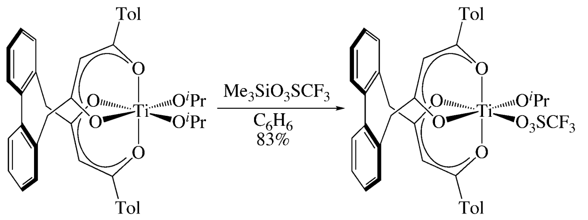
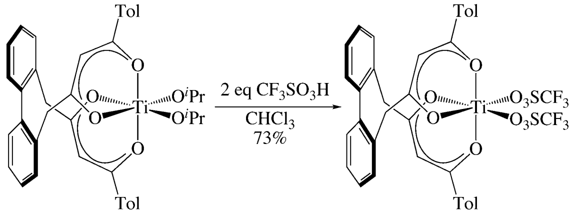
Schiff base complexes are also mixed, with usual (though not exclusive) formation of cis-α complexes of Ti and Zr[22] but a strong preference for the cis-*β* geometry in complexes of the later transition metals and main group elements.[23,29]

Furthermore, since the biphenyl moiety in the $R_2$Bob ligands has axial chirality, two diastereomers of the cis-α geometric isomer are possible. Only one diastereomer is ever observed by NMR, and crystallography indicates that it is the (*R*)-Λ/(*S*)-Δ diastereomer. Tight coupling of the biaryl chirality with the metal configuration is precedented in the studies of Scott on 2,2′-diaminobiaryl Schiff base ligands, where the (*R*)-Λ/(*S*)-Δ diastereomer is also formed quantitatively in cis-α complexes.[22] However, the apparent rigidity of the $R_2$Bob ligand contrasts with the behavior of bis(methylene)biphenyl-bridged bidentate phosphine ligands ("bisbi"), which show exceptional flexibility in binding. Despite having a "natural" bite angle of 113°,[30] the observed bite angles range from 101.76(3)° in a *cis*-$PtCl_2$ complex to 165.48(9)° in a *trans*-$NiCl_2$ complex.[31] Evidently the additional constraints imposed by the bidentate nature of the diketonates or by the necessarily transoid arrangement of Ti−O1−C2−C1 leads the $R_2$Bob ligands to have a very well-defined coordination geometry. In agreement with this structural rigidity is the lack of fluxionality of the ($R_2$Bob)Ti($O^iPr$)$_2$ complexes, as indicated for example by the sharp and diastereotopic methyl resonances of the isopropoxide groups. This indicates that these bis(diketonate) complexes, uniquely among known (dike)$_2$Ti(OR)$_2$ compounds, are optically stable, at least on the NMR time scale.

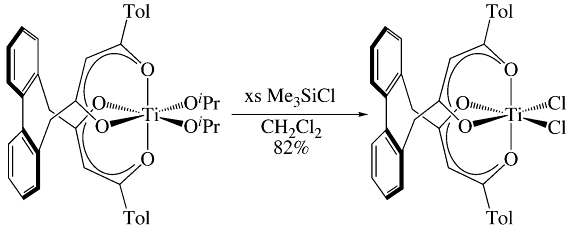
**Reactivity of ($Tol_2$Bob)Ti($O^iPr$)$_2$.** The $R_2$Bob ligands appear to have a high affinity for titanium(IV) and a strong propensity to remain mononucleating. Exposure of solutions of ($Tol_2$Bob)Ti($O^iPr$)$_2$ to moisture results in slow hydrolysis of the isopropoxides, forming mixtures of *μ*-oxo complexes, but the free diketonate is not lost from titanium. The isopropoxides can also be abstracted by Brønsted or Lewis acids. Thus, treatment of ($Tol_2$Bob)Ti($O^iPr$)$_2$ with 1 equiv of $Me_3SiO_3SCF_3$ results in the rapid release of $Me_3SiO^iPr$ and formation of the monoalkoxide complex ($Tol_2$Bob)Ti($O^iPr$)($O_3SCF_3$) (eq 4). The trifluoromethanesulfonate ligand is clearly covalently bound to the titanium, as indicated by the complex's $C_1$-symmetric NMR spectrum and by characteristic bands in the $^{19}$F NMR and IR spectra.[32] Replacement of the second alkoxide is more difficult and is incomplete even with an excess of $Me_3SiO_3SCF_3$. The sparingly soluble, dark red bis(triflate) complex is readily prepared, however, upon treatment of ($Tol_2$Bob)Ti($O^iPr$)$_2$ with two or more equivalents of triflic acid (eq 5). Both mono- and bis(triflate) complexes are prepared in high yield, with no sign of redistribution or dissociation of the bis(diketonate) ligand. This contrasts with the behavior of simple (dike)$_2$Ti(OR)$_2$, which are reported to form (dike)$_3$Ti$^+$ cations upon treatment with Lewis acids.[13b] Air-stable, sparingly soluble ($Tol_2$Bob)$TiCl_2$ can be prepared in good yield by treatment of ($Tol_2$Bob)Ti($O^iPr$)$_2$ with excess $Me_3SiCl$ (eq 6); the mixed alkoxy chloride complex ($Tol_2$Bob)Ti($O^iPr$)(Cl) can be observed by NMR as an intermediate in this reaction.



(4)

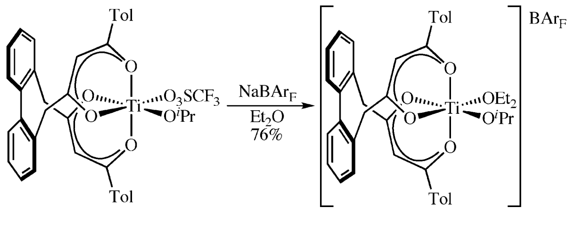


(5)



(6)

Even cationic species can be formed, which have never previously been accessible in bis(diketonate) titanium complexes. Treatment of ($Tol_2$Bob)Ti($O^iPr$)($O_3SCF_3$) with $NaBAr_F$ ($BAr_F$ = B[$C_6H_3$-3,5-($CF_3$)$_2$]$_4$) in dichloromethane, using an approach that has been used previously to generate reactive cationic complexes,[33] results in precipitation of sodium triflate. $^1$H NMR spectra taken in situ when the abstraction is performed in $CD_2Cl_2$ show the formation of a mixture of species, possibly *μ*-alkoxo complexes. If ether is added, or if the abstraction is performed in ether solution, then the cationic etherate [($Tol_2$Bob)Ti($O^iPr$)($OEt_2$)]$BAr_F$ can be isolated in good yield (eq 7).



(7)

The crystal structure of [($Tol_2$Bob)Ti($O^iPr$)($OEt_2$)]$BAr_F$ (Table 1, Figure 2) shows that it has the same ligand conformation and the same (*R*)-Λ/(*S*)-Δ configuration as ($^t$Bu$_2$Bob)Ti(O-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$. As expected for a coordina-

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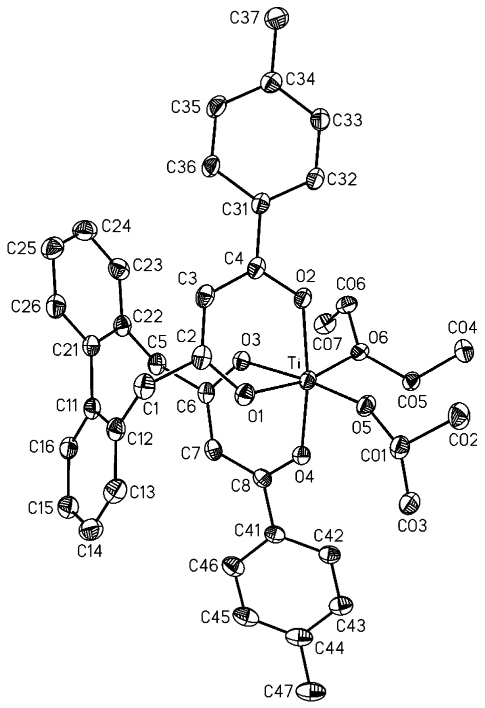

**Figure 2.** Thermal ellipsoid plot (40% ellipsoids) of the cation of [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$. Hydrogens are omitted for clarity.

tively saturated titanium(IV) center, there are no close contacts between the cation and the BAr$_F$ anion. The cationic titanium center exhibits shorter bond lengths than the neutral compound to both the diketonate oxygens (1.969 vs 2.025 Å av) and the alkoxide oxygen (1.7488(13) vs 1.8173(11) Å). This is consistent with its more electrophilic character, deriving both from its positive charge and its loss of a strongly $\pi$-donating alkoxide ligand. While the Ti−O$^i$Pr distance is very short and indicates substantial multiple bonding to titanium, it is actually slightly longer than those in neutral monoisopropoxide complexes Ti(O$^i$Pr)Cl$_3$L$_2$, which range from 1.702 to 1.726 Å.[34] The slight elongation of the Ti−O$^i$Pr bond in [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]$^+$, relative to other monoalkoxides, may be caused by the significant $\pi$-donation of the diketonates to titanium, which has been invoked in explaining the bonding[10] and spectroscopic properties[13b] of titanium diketonates. Neutral monomeric complexes with other strong $\pi$-donors, such as aryloxides or additional alkoxides, generally have Ti−O$^i$Pr distances in the range of 1.76−1.84 Å.[35] The ether oxygen is planar (sum of angles = 359.97°) and is among the shortest known titanium(IV)−diethyl ether linkages, which are typically in the range of 2.10−2.17 Å,[34a,36] with only the 2.0702(18) Å Ti−O bond in the imido-amido-triflate complex (ArN)(Ar-[$^t$BuCH═CMeCH═CMe]N)Ti(OTf)(OEt$_2$)[37] shorter than the 2.0878(14) Å Ti−ether bond observed here. The short bond to ether is also consistent with a highly electrophilic titanium center. There is a substantial trans effect, with the diketonate−titanium distance trans to the alkoxide 0.075 Å longer than the distance trans to the ether.

At temperatures below about 0 °C, the $^1$H and $^{13}$C{$^1$H} NMR spectra of [(Tol$_2$Bob)Ti(O$^i$Pr)(OEt$_2$)]BAr$_F$ are consistent with the crystallographically determined structure, with the resonances expected for a complex with $C_1$ symmetry. At these temperatures, free and bound Et$_2$O show distinct resonances. However, above 0 °C, the resonances for the free and bound ether broaden, indicating that exchange is taking place. The line width of the bound ether resonances is independent of the concentration of free Et$_2$O, suggesting that exchange is dissociative, and the barrier can be estimated, from the temperature of onset of fluxionality,[38] as ∼15 kcal/mol. Concurrent with the exchange of free and bound ether, the peaks from the inequivalent arms of the Tol$_2$Bob ligand exchange with each other, leading to time-averaged $C_2$ symmetry. Thus, the five-coordinate [(Tol$_2$Bob)Ti(O$^i$Pr)]$^+$ cation formed by dissociation of ether is either a trigonal bipyramid or a square pyramid in which the isopropoxy group moves from side to side more rapidly than ether recoordinates. Note that the resonances from the isopropoxy methyl groups remain sharp and diastereotopic during this fluxional process, indicating that exchange of O$^i$Pr groups between titanium centers is not rapid under these conditions. These observations, taken together, indicate that the R$_2$Bob ligand is compatible with a cationic, electrophilic titanium center somewhat reminiscent of a cationic group IV metallocene Cp$_2$M(X)$^+$ fragment.[39]

Although truly five-coordinate cations may prove difficult to isolate (as indicated, for example, by the mixtures observed when triflate is abstracted from(Tol$_2$Bob)Ti(O$^i$Pr)(OTf) in the absence of ether), the lability of the ether in [(Tol$_2$Bob)-Ti(O$^i$Pr)(OEt$_2$)]$^+$ indicates that such unsaturated cations are accessible enough to allow facile incorporation of neutral ligands into the coordination sphere. This opens the possibility of generating and using potentially reactive species such as an isopropoxy−ketone complex (as in the Meerwein−Ponndorf−Verley reductions)[40] or an enolate−alde-

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hyde complex (as in aldol condensations).[41] Titanium bis(diketonate) complexes have not previously been able to be used in these reactions because of their usual instability under Lewis acidic conditions.[13] The enhanced optical stability of the $(R_2Bob)Ti$ fragment compared to unlinked $(dike)_2Ti$ complexes also suggests the possibility of preparing optically active complexes and testing their efficacy in enantioselective reactions, giving the intriguing opportunity to observe whether the effects of electronic dissymmetry noted for the $(dike)_2Ti$ fragment in molecular recognition[10] will have parallels in chemical reactions. Efforts to explore the reactivity and selectivity of these electrophilic linked bis(diketonate) complexes are currently underway.

## Conclusions

For the first time, bis(diketones) capable of binding to a single metal center have been prepared. Both linker length and structure are critical in fostering structural specificity: A 2,2′-biphenyl linker appears to form a nine-membered ring that is too strained for a monotitanium complex to be stable, while the 11-membered ring formed by a 2,2′-tolan-bridged bis(diketonate) is sufficiently unstrained that a variety of geometric isomers are formed. In contrast, the 2,2′-bis(methylene)biphenyl-bridged ligands, $R_2Bob$, are extraordinarily selective in their structures, forming only monomers at equilibrium in their reactions with $Ti(O^iPr)_4$, only the cis-α isomers and only the (*R*)-Λ/(*S*)-Δ diastereomers. The stability of the $R_2Bob$ complexes allows the abstraction of alkoxides without redistribution or loss of the diketonates. This gives access to triflate and even cationic ether complexes of titanium ligated with diketones, which have been hitherto inaccessible using simple diketonate ligands.

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**Supporting Information Available:** Crystallographic information on $(^tBu_2Bob)Ti(O\text{-}2,6\text{-}^iPr_2C_6H_3)_2\cdot Et_2O$ and $[(Tol_2Bob)Ti(O^iPr)(OEt_2)]BAr_F$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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