Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 11458

www.rsc.org/dalton

PAPER

Redox-active tetrahydrosalen (salan) complexes of titanium†

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Received 28th June 2011, Accepted 8th August 2011
DOI: 10.1039/c1dt11228g

A diarylamino-substituted *N*-methyl tetrahydrosalen (salan) ligand, $^{An2N}LH_2$, is prepared in four steps and overall 53% yield from 5-bromosalicylaldehyde, with the key step a palladium-catalysed Hartwig–Buchwald amination of the *tert*-butyldimethylsilyl-protected 5-bromo-*N*-methylsalan ligand. Reaction of $^{An2N}LH_2$ or its bromo analogue with $Ti(O^iPr)_4$ or TiF_4 results in metalation of the ligand. The isopropoxide groups are readily exchanged with α- or β-hydroxyacids to form chelated complexes. X-ray crystallography and NMR spectroscopy indicate that the salan ligands are quite flexible, with $^{An2N}LTiF_2$, for example, showing four stereoisomers in its ^{19}F NMR spectrum. The major stereoisomer of (salan)Ti(X)(Y) depends principally on the *trans* influence of the X and Y groups. Complexes of ^{An2N}L show two reversible, closely spaced redox couples at approximately + 0.1 V *vs.* ferrocene/ferrocenium, and a second set of two closely spaced redox couples at ~ + 0.8 V *vs.* Fc/Fc^+.

Introduction

Bis(salicylidene)ethylenediamine (salen) ligands and their saturated analogues (salan) are an important class of tetradentate dianionic ligands that have been used extensively in transition metal chemistry.[1] While they are most typically used as chemically inert supporting ligands, a number of late-metal salen and salan complexes have been observed to undergo outer-sphere oxidation to form stable complexes of aroxyl radicals,[2] with particularly electron-rich examples showing very facile oxidation.[3] Oxidized copper salen and salan complexes in particular have been studied for their ability to mediate the oxidation of alcohols, by analogy to the enzyme galactose oxidase.[4]

Aryloxide complexes of the early transition metals are markedly more difficult to oxidize than those of the later transition metals due to the strong metal–oxygen π bonding exhibited by these metals.[5] Thus, while salen and salan complexes of titanium have been used as catalysts for oxidation reactions, these reactions have relied on the Lewis acidity of titanium to activate oxidants such as hydrogen peroxide rather than the ability of the ligands (or metal) to undergo redox reactions.[6,7] A ferrocenylethynyl–salen titanium complex has been observed to show activity for polymerization of lactones that is modulated by the redox state of the ferrocenes, but that effect was attributed to a change in inductive effects,[8] consistent with observations in other systems that oxidation of remote ferrocenes produces only small orbital perturbations at titanium.[9]

We recently reported the preparation of tripodal ligands $N(CH_2C_6H_2\text{-}3\text{-}R\text{-}5\text{-}N[C_6H_4OMe]_2\text{-}2\text{-}OH)_3$ (R = H, ^{t}Bu) containing *para*-diarylaminophenol groups.[10] Titanium binds readily to this ligand and forms complexes that show six reversible oxidation reactions. Here we describe the preparation of an analogous salan ligand, its metalation by titanium, and the electrochemical properties of the metal complexes.

Experimental

General procedures

Unless otherwise noted, all procedures were carried out inside a drybox or using vacuum line techniques. Chlorinated solvents were dried over 4 Å molecular sieves, followed by CaH_2. Benzene was dried over sodium. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and were stored in the drybox prior to use. All other reagents were commercially available and used without further purification. NMR spectra were measured on a Varian VXR-300 or VXR-500 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra are reported in ppm downfield of TMS, using the known chemical shifts of the solvent residuals. Chemical shifts for ^{19}F NMR spectra are reported in ppm downfield of $CFCl_3$. Infrared spectra were recorded as Nujol mulls on NaCl plates on a Nicolet 670 FT-IR spectrometer and are reported in cm^{-1}. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer. Samples were analyzed either by first flushing the system with MeOH–CH_2Cl_2–0.5% formic acid and then introducing the samples into the ion source by direct flow of a solution of the analyte in anhydrous CH_2Cl_2 with a flow rate of 10 μL min^{-1} in fast-forward mode, or by first flushing the source with isopropanol and introducing the sample into the source by direct flow of a solution of the analyte in anhydrous isopropanol

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† CCDC reference numbers 832123–832125. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11228g

at 20 μL min^{-1}. FAB mass spectra were obtained on a JEOL LMS-AX505HA mass spectrometer using 3-nitrobenzyl alcohol or nitrophenyl octyl ether as a matrix. Peaks reported are the mass number of the most intense peak of isotope envelopes. UV-visible spectra were measured in dichloromethane solutions (except as noted) in 1-cm screw cap quartz cuvettes using a Beckman DU-7500 diode array spectrophotometer, and are reported as λ_{max}/nm (ε/$M^{-1}cm^{-1}$). Elemental analyses were performed either by M-H-W Laboratories (Phoenix, AZ) or Midwest Microlab, LLC (Indianapolis, IN).

Ligand synthesis

***N*,*N*′-Bis(2-hydroxo-5-bromobenzyl)ethylenediamine.** To a stirred solution of 13.08 g 5-bromosalicylaldehyde (Aldrich, 65.1 mmol) in 300 mL methanol in the air was slowly added a solution of 1.95 g (32.5 mmol) ethylenediamine in methanol (15 mL). The solution turned bright yellow as the amine addition proceeded and deposited a yellow precipitate. After stirring the slurry for 5 min, 4.95 g solid $NaBH_4$ (131 mmol) was added in small portions over 40 min. The color of the reaction mixture decreased in intensity as the borohydride addition proceeded, with the bright yellow precipitate dissolving and a pale yellow precipitate forming. After stirring overnight, the pale yellow solid was isolated by suction filtration, washed with 2 × 15 mL methanol, and air-dried for 1 h to yield 12.74 g of the bromo-substituted diamine (91%). Mp 160–162° (lit.[11] 175–176°). ^{1}H NMR ($CDCl_3$): δ 2.83 (s, 4H, NCH_2CH_2N), 3.96 (s, 4H, ArCH_2N), 6.72 (d, 9 Hz, 2H, Ar 3-H), 7.10 (d, 3 Hz, 2H, Ar 6-H), 7.26 (dd, 9, 3 Hz, 2H, Ar 4-H). The compound is too insoluble for ^{13}C NMR analysis. IR (cm^{-1}): 3421 (br, ν_{OH}), 3270 (m, ν_{NH}), 2410 (br), 1585 (m), 1413 (m), 1296 (m), 1274 (s), 1255 (m), 1202 (s), 1178 (m), 1115 (s), 1076 (m), 1017 (w), 945 (m), 937 (m), 888 (s), 851 (w), 829 (vs), 777 (m), 723 (s), 628 (s).

***N*,*N*′-Dimethyl-*N*,*N*′-Bis(2-hydroxo-5-bromobenzyl)ethylenediamine, ^{Br}LH$_2$.** To a stirred mixture of 5.82 g *N*,*N*′-bis(2-hydroxo-5-bromobenzyl)ethylenediamine (13.5 mmol), 175 mL CH_3CN and 30 mL glacial acetic acid in a 500 mL Erlenmeyer flask in the air was added 11 mL 37% aqueous formaldehyde (400 mmol, 15 equiv). After stirring for 40 min, 2.23 g solid $NaBH_4$ (58.9 mmol, 2.2 equiv) was added in portions over 10 min. The mixture warms and eventually becomes turbid. After stirring overnight, the cloudy mixture was poured into a round-bottom flask, the Erlenmeyer rinsed with 15 mL H_2O, and the rinse combined with the reaction mixture. The volume of the mixture was reduced to 75 mL on the rotary evaporator. To the stirred mixture was slowly added 10% aqueous NaOH until the pH was neutral (~80 mL). After stirring for 10 min to allow the effervescence to cease, the mixture was suction filtered and the white solid washed with 2 × 20 mL H_2O, then 2 × 30 mL CH_3OH, then air-dried for 15 min to furnish 5.93 g ^{Br}LH$_2$ (96%). ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 6H, NCH_3), 2.64 (s, 4H, NCH_2CH_2N), 3.66 (s, 4 H, ArCH_2N), 6.72 (d, 9 Hz, 2H, Ar 3-H), 7.07 (d, 2.5 Hz, 2H, Ar 6-H), 7.26 (dd, 9, 2.5 Hz, 2H, Ar 4-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 41.85 (NCH_3), 54.08 (NCH_2CH_2N), 61.47 (ArCH_2N), 111.08, 118.31, 123.71, 131.28, 131.93, 157.17. IR (Nujol mull, cm^{-1}): 2600 (v br, ν_{OH}), 1877 (w), 1643 (w), 1602 (s), 1578 (s), 1524 (w), 1412 (m), 1295 (s), 1255 (s, br), 1196 (s), 1178 (m), 1164 (w), 1132 (m), 1115 (m), 1099 (s), 1074 (s), 1019 (s), 973 (s), 939 (w), 915 (m), 878 (s), 847 (m), 821 (s), 793 (w), 761 (s), 719 (w), 649 (s), 625 (s), 550 (m). Anal. Calcd for $C_{18}H_{22}Br_2N_2O_2$: C, 47.19; H, 4.84; N, 6.11. Found: C, 47.16; H, 4.63; N, 5.84.

***N*,*N*′-Dimethyl-*N*,*N*′-bis(2-(*tert*-butyldimethylsiloxy)-5-bromobenzyl)ethylenediamine dihydrochloride.** In the air, ^{Br}LH$_2$ (3.09 g, 6.74 mmol), *tert*-butyldimethylsilyl chloride (3.06 g, Acros, 20.3 mmol, 3.02 equiv), 60 mL CH_2Cl_2, and a stirbar were added to a round-bottom flask. The flask was sealed with a rubber septum, and through the septum 3.05 mL DBU (20.4 mmol, 3.02 equiv) was added *via* syringe over 3 min. After stirring for 30 min, the mixture was poured into a separatory funnel and shaken with 75 mL 1 M aqueous HCl. The cloudy organic layer was drained into a round-bottom flask, reduced in volume to about 10 mL on the rotary evaporator, and poured into 80 mL ether, causing a voluminous white precipitate to form. The precipitate was suction filtered on a glass frit, washed thoroughly with 2 × 20 mL ether, and air-dried for 20 min to give 4.75 g (93%) of the protected amine dihydrochloride. ^{1}H NMR (CD_2Cl_2): δ 0.30 (s, 12H, Si(CH_3)$_2$), 1.01 (s, 18H, SiC(CH_3)$_3$), 2.75 (s, 6H, NCH_3), 3.83 (br s, 4H, NCH_2CH_2N), 4.29 (br s, NCH_2Ar), 6.81 (d, 9 Hz, 2H, Ar 3-H), 7.43 (dd, 9, 3 Hz, 2H, Ar 4-H), 8.03 (d, 3 Hz, 2H, Ar 6-H), 12.77 (v br s, 2H, N*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ –3.74 (Si(*C*H_3)$_2$), 18.81 (Si*C*(CH$_3$)$_3$), 26.28 (SiC(*C*H_3)$_3$), 39.55 (v br), 50.80 (br), 54.45 (v br), 114.20, 121.19, 121.79, 135.05, 136.69, 154.78. IR: 3420 (m, br, ν_{NH}), 2322 (m, br), 1487 (s), 1405 (w), 1282 (s), 1263 (s), 1184 (w), 1132 (m), 945 (w), 917 (m), 906 (m), 861 (s), 846 (s), 832 (m), 805 (m), 782 (s), 671 (w). ESI-MS: 687.1843 ((M+H)$^+$, calcd 687.1833). Anal. Calcd for $C_{30}H_{52}Br_2Cl_2N_2O_2Si_2$: C, 47.43; H, 6.90; N, 3.69. Found: C, 46.38; H, 7.10; N, 3.40.

***N*,*N*′-Dimethyl-*N*,*N*′-Bis(2-hydroxo-5-(di-(4-methoxyphenyl)-amino)benzyl)ethylenediamine, ^{An2N}LH$_2$.** Into a 50-mL Erlenmeyer flask in the air was weighed 1.1005 g *N*,*N*′-dimethyl-*N*,*N*′-bis(2-(*tert*-butyldimethylsiloxy)-5-bromobenzyl)ethylenediamine dihydrochloride (1.45 mmol). The solid was dissolved in 30 mL CH_2Cl_2 and shaken with 25 mL 5% aqueous NaOH in a separatory funnel. The dichloromethane layer was drained off and the aqueous layer washed with 10 mL additional CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and stripped down on the rotary evaporator to yield a pale yellow oil.

This oil was taken directly into the drybox. In the box, 663.1 mg 4,4′-dimethoxydiphenylamine (Alfa-Aesar, 2.89 mmol, 2.00 equiv), 416.9 mg sodium *tert*-butoxide (Aldrich, 4.34 mmol, 2.99 equiv) and 47.5 mg $Pd_2(dba)_3$ (Strem, 0.104 mmol Pd, 7 mol%) were weighed into a 20-mL scintillation vial. The free-base aryl bromide was dissolved in ~12 mL benzene and added to the solid reagents. A solution of 16.6 mg tri-*tert*-butyl phosphine (Strem, 0.082 mmol, 5.6 mol%) in ~3 mL benzene was then added to this mixture. A stirbar was added, the vial sealed with a Teflon-lined screw-cap, and the reaction mixture taken out of the drybox and stirred at room temperature overnight.

After 17 h, the mixture was opened in the air and poured into 10 mL saturated aqueous ammonium chloride solution, and the reaction flask washed with a few mL ether, which was added to the organic/aqueous mixture. The organic/aqueous mixture was stirred for 5 min; it rapidly turned dark red-brown and palladium black was deposited. The layers were then separated in a separatory funnel, the organic layer dried over $MgSO_4$, filtered,

and stripped down on the rotary evaporator to give the silyl-protected compound as a brown oil.

The oil was extracted into 15-mL portions of methanol, requiring ~90 mL methanol total. To the methanol solution was added a stirbar and 0.5 g ammonium fluoride (Alfa-Aesar, 13.5 mmol, 4.5 equiv per silyl group) and the mixture stirred vigorously overnight at room temperature. Within an hour, the product had begun to precipitate as a tan solid. After stirring overnight, the solid was collected by suction filtration, washed thoroughly first with 10 mL H_2O, then 2 × 15 mL methanol, then air-dried for 1 h to yield 0.714 g $^{An2N}LH_2$ (65%). ^{1}H NMR (C_6D_6): δ 1.73 (s, 6H, NCH_3), 2.02 (s, 4H, NCH_2CH_2N), 2.99 (s, 4H, ArCH_2N), 3.28 (s, 12H, OCH_3), 6.73 (d, 9 Hz, 8H, NC_6H_4OMe 2,6-H), 6.80 (d, 2 Hz, 2H, Ar 6-H), 6.97 (d, 9 Hz, 2H, Ar 3-H), 7.01 (dd, 9, 2 Hz, 2H, Ar 4-H), 7.10 (d, 9 Hz, 8H, NC_6H_4OMe 3,5-H). ^{13}C{^{1}H} NMR (C_6D_6): δ 41.70 (NCH_3), 54.29 (NCH_2CH_2N), 55.42 (OCH_3), 61.77 (NCH_2Ar), 115.40, 117.87, 123.22, 125.27, 125.54, 125.74, 141.44, 143.20, 154.63, 155.95. IR: 1606 (w), 1508 (s), 1493 (s), 1327 (w), 1302 (w), 1283 (w), 1245 (s), 1181 (w), 1104 (m), 1039 (s), 983 (m), 866 (w), 836 (s), 728 (s). ESI-MS: 755.3817 (M+H$^+$, calcd 755.3803). Anal. Calcd for $C_{46}H_{50}N_4O_6$: C, 73.19; H, 6.68; N, 7.42. Found: C, 73.03; H, 6.65; N, 7.29.

Metalation of salan ligands

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-bromobenzyl)ethylenediamine]titanium(IV) diisopropoxide, ^{Br}LTi(O^{i}Pr)$_2$. To a suspension of the ligand $^{Br}LH_2$ (0.8000 g, 1.75 mmol) in benzene (10 mL) was added a solution of Ti(O^{i}Pr)$_4$ (Aldrich, 0.4962 g, 1.75 mmol) in 10 mL benzene dropwise with vigorous stirring. The initial pinkish-white suspension became translucent yellow after the addition was completed. Stirring was stopped after 35 min, and the volatiles were evaporated under vacuum to give a pale yellow foam. The residue was triturated with 10 mL hexane and allowed to stand for 10 min. The precipitate was filtered on a glass frit, washed with hexanes (2 × 10 mL), and dried. Yield 0.8843 g (81%). ^{1}H NMR ($CDCl_3$): δ 1.24 (d, 6 Hz, 6H, CH(CH_3)(CH′$_3$)), 1.23 (d, 6 Hz, 6H, CH(CH$_3$)(CH'_3)), 1.84 (pseudo-d, 10 Hz, 2H, NCHH′CHH′N), 2.43 (s, 6H, NCH_3), 2.97 (pseudo-d, 9 Hz, 2H, NCHH'CHH'N), 3.09 (d, 14 Hz, 2H, NCHH′Ar), 4.58 (d, 14 Hz, 2H, NCHH'Ar), 4.97 (sept, 6 Hz, 2H, CH(CH$_3$)$_2$), 6.55 (d, 9 Hz, 2H, Ar 3-H), 7.07 (d, 2.5 Hz, 2H, Ar 6-H), 7.24 (dd, 9, 3 Hz, 2H, Ar 4-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.82 (OCH(CH_3)(CH′$_3$)), 26.12 (OCH(CH$_3$)(CH'_3)), 47.39 (NCH_3), 51.97 (NCH_2CH_2N), 63.97 (NCH_2Ar), 78.62 (OCH(CH$_3$)$_2$), 108.98, 119.59, 126.48, 132.03, 132.07, 161.22. IR: 1586 (m), 1560 (m), 1406 (s), 1363 (s), 1302 (m), 1290 (s), 1185 (w), 1163 (m), 1118 (s), 1074 (w), 1053 (w), 980 (m), 961 (w), 944 (w), 900 (m). UV-vis: 303 (2.2 × 10^4). ESI-MS: 562.9872 ((M–O^{i}Pr)$^+$, calcd 562.9847). Anal. Calcd for $C_{24}H_{34}Br_2N_2O_4Ti$: C, 46.33; H, 5.51; N, 4.50. Found: C, 46.40; H, 5.40; N, 4.36.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-(di-(4-methoxyphenyl)-amino)benzyl)-ethylenediamine]titanium(IV) diisopropoxide, ^{An2N}LTi(O^{i}Pr)$_2$. $^{An2N}LH_2$ (0.5000 g, 0.662 mmol) was reacted with Ti(O^{i}Pr)$_4$ as described above for the bromo analogue to yield 0.5169 g (85%) of ^{An2N}LTi(O^{i}Pr)$_2$. ^{1}H NMR ($CDCl_3$): δ 1.24 (d, 6 Hz, 6H, CH(CH_3)(CH′$_3$)), 1.30 (d, 6 Hz, 6H, CH(CH$_3$)(CH'_3)) 1.85 (pseudo-d, 9 Hz, 2H, NCHH′CHH′N), 2.45 (s, 6H, NCH_3), 3.00 (d, 14 Hz, NCHH′Ar), 3.04 (pseudo-d, 10.5 Hz, 2H, NCHH'CHH'N), 3.79 (s, 12H, OCH_3), 4.59 (d, 13 Hz, 2H, NCHH'Ar), 5.10 (sept, 6 Hz, 2H, CH(CH$_3$)$_2$), 6.55 (d, 8.5 Hz, 2H, Ar 3-H), 6.68 (d, 2 Hz, 2H, Ar 6-H), 6.78 (d, 9 Hz, 8H, $NC_6H_4OCH_3$ 2,6-H), 6.87 (dd, 8.5, 2.5 Hz, 2H, Ar 4-H), 6.97 (d, 9 Hz, 8 H, $NC_6H_4OCH_3$ 3,5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.87 (OCH(CH_3)(CH′$_3$), 26.20 (OCH(CH$_3$)(CH'_3)), 47.41 (NCH_3), 51.94 (NCH_2CH_2N), 55.72 (OCH_3), 64.49 (NCH_2Ar), 78.01 (OCH(CH$_3$)$_2$), 114.56, 118.19, 124.46, 125.50, 125.83, 139.06, 142.59, 154.67, 158.05. IR: 1604 (w), 1503 (w), 1419 (m), 1302 (m), 1273 (s), 1239 (s), 1180 (w), 1161 (w), 1109 (w), 1039 (s), 997 (w), 967 (w), 886 (s), 811 (m), 800 (m), 774 (w), 728 (s), 667 (m), 559 (w). UV-vis: 365 (3.1 × 10^4), 299 (5.5 × 10^4). ESI-MS: 918.4064 (M$^+$, calcd 918.4047). Anal. Calcd for $C_{52}H_{62}N_4O_8Ti$: C, 67.97; H, 6.80; N, 6.10. Found: C, 67.85; H, 6.70; N, 5.89.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-(di-(4-methoxyphenyl)-amino)benzyl)-ethylenediamine]titanium(IV) difluoride, ^{An2N}LTiF$_2$. $^{An2N}LH_2$ (0.1000 g, 0.115 mmol), TiF_4 (Strem, 0.0284 g, 0.229 mmol), CH_2Cl_2 (10 mL), and a stir bar were placed in a 20 mL scintillation vial. The vial was tightly sealed with a Teflon-lined screw cap and the mixture heated with vigorous stirring in a 70 °C oil bath for 16 h. The reaction mixture was cooled, filtered on a glass frit under nitrogen to remove unreacted titanium tetrafluoride, and the residue washed with CH_2Cl_2 (5 mL). The combined filtrates were dried under vacuum to give a sticky dark red solid. The solid was slurried with hexanes (20 mL) and filtered on a glass frit. After drying under vacuum for 1 h, the yield of red difluoride complex was 0.0298 g (31%). ^{1}H NMR (CD_2Cl_2, major isomer, added Cp*$_2$Fe): δ 2.15 (s, 3H, NCH_3), 2.21 (d, 13 Hz, 1H, NCH$_2$CHH'N), 2.40 (d, 11 Hz, 1H, NCHH′CH$_2$N), 2.82 (d, $^4J_{FH}$ = 4 Hz, 3H, NCH_3), 3.06 (t, 14 Hz, 1H, NCH$_2$CHH′N), 3.12 (d, 12.5 Hz, 1H, NCHH′Ar), 3.27 (d, 14.5 Hz, 1H, NCHH'Ar), 3.51 (t, 14 Hz, 1H, NCHH'CH$_2$N), 3.76 (s, 12H, OCH_3), 4.43 (d, 14 Hz, 1H, NCHH'Ar), 4.70 (d, 13 Hz, 1H, NCHH'Ar), 6.45 (d, 9 Hz, 1H, Ar 3-H), 6.57 (d, 9 Hz, 1H, Ar 3-H), 6.74–6.80 (m, 12H, ArH and $NC_6H_4OCH_3$ 2,6-H), 6.96 (d, 9 Hz, 8H, $NC_6H_4OCH_3$ 3,5-H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 43.79 (NCH_3), 48.93 (d, 14 Hz), 52.63 (NCH_3), 55.95 (OCH_3), 57.97 (NCH_2CH_2N), 63.99 (NCH$_2$CH_2N), 64.77 (d, 9 Hz), 115.00 (2C, $NC_6H_4OCH_3$ 2,6-C), 115.93, 116.96, 123.64, 124.12, 124.16, 124.42, 125.69, 125.80 (2C, $NC_6H_4OCH_3$ 3,5-C), 126.30, 142.10 (2C, $NC_6H_4OCH_3$ 1-C), 142.42, 143.02, 155.43, 155.83 (2C, $NC_6H_4OCH_3$ 4-C), 156.16. ^{19}F NMR (CD_2Cl_2): δ 100.15 (d, 40 Hz, *cis*-β-*trans*-NCH$_3$, F *trans* to N), 103.07 (s, *trans*-α), 103.62 (d, 36 Hz, *cis*-β-*cis*-NCH$_3$, F *trans* to N), 146.39 (d, 40 Hz, *cis*-β-*trans*-NCH$_3$, F *trans* to O), 150.36 (d, 36 Hz, *cis*-β-*cis*-NCH$_3$, F *trans* to O), 168.48 (s, *cis*-α). IR: 1499 (w), 1461 (vs), 1377 (s), 1232 (s), 1176 (w), 1102 (w), 1029 (m), 888 (m), 813 (m), 776 (w), 721 (m). UV-vis: 421 (2.1 × 10^4), 297 (5.7 × 10^4). ESI-MS: 838.3024 (M$^+$, calcd 838.3021). Anal. Calcd for $C_{46}H_{48}F_2N_4O_6Ti$: C: 65.87; H, 5.77; N, 6.68. Found: C, 65.78; H, 5.86; N, 6.49.

Exchange of ancillary ligands

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-bromobenzyl)](2-methyl-2-oxidopropanoato)titanium(IV), ^{Br}LTi(OC(CH$_3$)$_2$C(O)O). ^{Br}LTi(O^{i}Pr)$_2$ (0.1500 g, 0.241 mmol) and α-hydroxyisobutyric acid (Aldrich, 0.0251 g, 0.241 mmol) were dissolved in chloroform (5 mL each). The α-hydroxyisobutyric acid solution was added dropwise to the titanium precursor with vigorous stirring,

yielding a yellow solution. Stirring was stopped after 15 min, and the volatiles were evaporated under vacuum. The pale yellow solid was suspended in hexanes (20 mL), filtered through a frit, and vacuum dried overnight to give 0.1380 g product (94%). ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 3H, OC(O)C(CH_3)(CH′$_3$)O), 1.40 (s, 3H, OC(O)C(CH$_3$)(CH'_3)O), 2.08 (s, 3H, NCH_3), 2.24 (dd, 13, 2.5 Hz, 1H, NCH$_2$CHHN), 2.45 (dd, 13, 2.5 Hz, 1H, NCHHCH$_2$N), 2.83 (s, 3H, NCH_3), 3.02 (td, 13, 2.5 Hz, 1H, NCH$_2$CHHN), 3.18 (d, 13.5 Hz, 1H, NCHH′Ar), 3.48 (d, 14 Hz, 1H, NCHH′Ar), 3.59 (td, 13, 2.5 Hz, 1H, NCHHCH$_2$N), 4.66 (d, 14 Hz, 1H, NCHH'Ar), 5.00 (d, 13.5 Hz, 1H, NCHH'Ar), 6.61 (d, 8.5 Hz, 1H, Ar 3-H), 6.65 (d, 8.5 Hz, 1H, Ar 3-H), 7.13 (d, 2 Hz, 1H, Ar 6-H), 7.28 (d, 2 Hz, 1H, Ar 6-H), 7.30 (dd, 9, 3 Hz, 1H, Ar 4-H), 7.34 (dd, 9, 2.5 Hz, 1H, Ar 4-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.48 (OC(O)C(CH_3)(CH′$_3$)O), 27.63 (OC(O)C(CH$_3$)(CH'_3)O), 42.85 (NCH_3), 50.84 (NCH_3), 52.12 (NCH_2CH$_2$N), 57.23 (NCH$_2$CH_2N), 63.46 (NCH_2Ar), 63.85 (NCH_2Ar), 94.31 (OC(O)C(CH$_3$)$_2$O), 112.41, 113.20, 118.00, 118.40, 125.84, 127.10, 131.75, 132.24, 132.61, 133.31, 159.35, 159.83, 186.66 (C(O)O). IR: 1685 (m, $\nu_{C=O}$), 1410 (w), 1268 (s), 1192 (m), 1121 (w), 973 (w), 820 (m), 723 (m), 675 (m). UV-vis: 334 (2.4×10^4), 301 (1.9×10^4). FAB-MS: 605 (M+H$^+$). Anal. Calcd for $C_{22}H_{26}Br_2N_2O_5Ti$: C, 43.59; H, 4.32; N, 4.62. Found: C, 43.33; H, 4.29; N, 4.43.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-bromobenzyl)ethylenediamine](2,2-dimethyl-3-oxidopropanoato)titanium(IV), ^{Br}LTi(OCH$_2$C(CH$_3$)$_2$C(O)O). ^{Br}LTi(O^{i}Pr)$_2$ (0.1500 g, 0.241 mmol) and hydroxypivalic acid (Aldrich, 0.0285 g, 0.241 mmol) were reacted as described for the α-hydroxyisobutyrate derivative to yield 0.1330 g (89%) of the hydroxypivalate complex. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 3H, C(CH_3)(CH′$_3$)), 1.40 (s, 3H, C(CH$_3$)(CH'_3)), 2.13 (s, 3H, NCH_3), 2.21 (dd, 14, 2 Hz, 1H, NCHH′CH$_2$N), 2.38 (dd, 13, 2 Hz, 1H, NCH$_2$CHH′N), 2.77 (s, 3H, NCH_3), 3.03 (td, 13, 2 Hz, 1H, NCHH'CH$_2$N), 3.11 (d, 14 Hz, 1H, NCHH'Ar), 3.40 (d, 14 Hz, 1H, NCHH′Ar), 3.69 (td, 13, 3 Hz, 1H, NCH$_2$CHH'N), 3.89 (d, 12 Hz, 1H, NCHH'Ar), 4.51 (d, 12 Hz, 1H, NCHH'Ar), 4.58 (d, 13 Hz, 1H, OC(O)C(CH$_3$)$_2$CHH′O), 4.99 (d, 14 Hz, 1H, OC(O)C(CH$_3$)$_2$CHH'O), 6.57 (d, 8.5 Hz, 1H, Ar 3-H), 6.65 (d, 8.5 Hz, 1H, Ar 3-H), 7.13 (d, 2 Hz, 1H, Ar 6-H), 7.24 (d, 2 Hz, 1H, Ar 6-H), 7.29 (dd, 7, 2 Hz, 1H, Ar 4-H), 7.32 (dd, 9, 2.5 Hz, 1H, Ar 4-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.63 (C(CH_3)(CH′$_3$)), 24.08 (C(CH$_3$)(CH'_3)), 43.31 (OC(O)C(CH$_3$)$_2$CH$_2$O), 43.36 (NCH_3), 50.50 (NCH_3), 52.74 (NCH$_2$CH_2N), 56.79 (NCH_2CH$_2$N), 63.52 (NCH_2Ar), 64.07 (NCH_2Ar), 83.98 (OC(O)C(CH$_3$)$_2$CH_2O), 112.34, 112.38, 118.21, 118.63, 126.38, 126.80, 131.80, 132.05, 132.48, 133.18, 159.54, 159.67, 180.65 (TiOC(O)). IR: 1653 (s, $\nu_{C=O}$), 1408 (m), 1261 (m), 1170 (m), 1119 (w), 1064 (m), 894 (w), 814 (m), 721 (w), 676 (s). UV-vis: 332 (2.3×10^4), 303 (1.7×10^4). FAB-MS: 619 (M+H$^+$). Anal. Calcd for $C_{23}H_{28}Br_2N_2O_5Ti$: C, 44.54; H, 4.55; N, 4.52. Found: C, 44.65; H, 4.33; N, 3.48.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-(di-(4-methoxyphenyl)-amino)benzyl)ethylenediamine](2-methyl-2-oxidopropanoato)titanium(IV), ^{An2N}LTi(OC(CH$_3$)$_2$C(O)O). The compound was prepared as described for the bromosalan analogue using ^{An2N}LTi(O^{i}Pr)$_2$ (0.1500 g, 0.163 mmol) to give 0.1180 g (79%) of the chelated product. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 3H, OC(O)C(CH_3)(CH′$_3$)O), 1.63 (s, 3H, OC(O)C(CH$_3$)(CH'_3)O), 2.14 (d, 12 Hz, 1H, NCH$_2$CHH′N), 2.20 (s, 3H, NCH_3), 2.40 (d, 12 Hz, 1H, NCHH′CH$_2$N), 2.75 (s, 3H, NCH_3), 3.11 (d, 14 Hz, 1H, NCHH'Ar), 3.10 (t, 11 Hz, 1H, NCH$_2$CHH'N), 3.34 (d, 14 Hz, 1H, NCHH′Ar), 3.52 (t, 11 Hz, 1H, NCHH'CH$_2$N), 3.79 (s, 12H, OCH_3), 4.63 (d, 14 Hz, 1H, NCHH'Ar), 4.92 (d, 14 Hz, 1H, NCHH′Ar), 6.58 (d, 9 Hz, 1H, Ar 3-H), 6.61 (d, 9 Hz, 1H, Ar 3-H), 6.67 (d, 2 Hz, 1H, Ar 6-H), 6.77-6.84 (m, 3H, ArH), 6.79 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 2,6-H), 6.80 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 2,6-H), 6.98 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H), 6.99 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.74 (OC(O)C(CH_3)(CH′$_3$)O), 27.92 (OC(O)C(CH$_3$)(CH'_3)O), 43.21 (NCH_3), 50.48 (NCH_3), 51.99 (NCH_2CH$_2$N), 55.71 (OCH_3), 57.40 (NCH$_2$CH_2N), 64.15 (NCH_2Ar), 64.58 (NCH_2Ar), 92.78 (OC(O)C(CH$_3$)$_2$O), 114.73, 114.84, 116.55, 117.01, 123.52, 123.59, 123.85, 124.58, 125.31, 125.42, 125.74, 125.98, 141.64, 141.88, 142.05, 142.70, 155.22, 155.59, 156.29, 187.07 (C=O). IR: 1676 (s, $\nu_{C=O}$), 1604 (w), 1504 (sh), 1489 (sh), 1300 (w), 1262 (w), 1239 (s), 1197 (w), 1120 (w), 1034 (m), 979 (w), 887 (s), 823 (s), 781 (m), 729 (s), 664 (w). UV-vis: 405 (2.6×10^4), 297 (7.1×10^4). FABMS: 903 (M$^+$). Anal. Calcd for $C_{50}H_{54}N_4O_9Ti$: C, 66.52; H, 6.03; N, 6.21. Found: C, 66.46; H, 6.01; N, 5.98.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-(di-(4-methoxyphenyl)-amino)benzyl)ethylenediamine](2,2-dimethyl-3-oxidopropanoato)titanium(IV), ^{An2N}LTi(OCH$_2$C(CH$_3$)$_2$C(O)O). The compound was prepared from ^{An2N}LTi(O^{i}Pr)$_2$ (0.1500 g, 0.163 mmol) and hydroxypivalic acid (0.0193 g, 0.163 mmol) using the same procedure employed for the α-hydroxybutyrate compound to yield 0.1264 g (84%) of the hydroxypivalate complex. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 3H, OCH$_2$C(CH_3)(CH′$_3$)C(O)O), 1.44 (s, 3H, OCH$_2$C(CH$_3$)(CH'_3)C(O)O), 2.11 (d, 12 Hz, 1H, NCH$_2$CHH′N), 2.21 (s, 3H, NCH_3), 2.70 (d, 12 Hz, 1 H, NCHHCH$_2$N), 2.69 (s, 3H, NCH_3), 3.01 (d, 13.5 Hz, 1H, NCHH′Ar), 3.11 (t, 13 Hz, 1H, NCH$_2$CHH'N), 3.28 (d, 14 Hz, 1H, NCHH′Ar), 3.63 (t, 13 Hz, 1H, NCHH'CH$_2$N), 3.79 (s, 12H, OCH_3), 3.89 (d, 12 Hz, 1H, NCHH'Ar), 4.45 (d, 12 Hz, 1H, NCHH'Ar), 4.53 (d, 13 Hz, 1H, OCHH′C(CH$_3$)$_2$C(O)O), 4.92 (d, 13 Hz, 1H, OCHH'C(CH$_3$)$_2$C(O)O), 6.55 (d, 8.5 Hz, 1H, Ar 3-H), 6.60 (d, 8.5 Hz, 1H, Ar 3-H), 6.66 (d, 2.5 Hz, 1H, Ar 6-H), 6.74 (d, 3 Hz, Ar 6-H), 6.79-6.85 (m, 10H, NC$_6$H$_4$OCH$_3$ 2,6-H and Ar 4-H), 6.97 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H), 6.99 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.86 (OC(O)C(CH_3)(CH′$_3$)O), 24.26 (OC(O)C(CH$_3$)(CH'_3)O), 43.47 (OCH$_2$C(CH$_3$)$_2$C(O)O), 43.56 (NCH_3), 50.19 (NCH_3), 52.65 (NCH$_2$CH_2N), 55.72 (OCH_3), 56.92 (NCH$_2$CH_2N), 64.11 (NCH_2Ar), 64.71 (NCH_2Ar), 83.23 (OCH_2C(CH$_3$)$_2$C(O)O), 114.73, 114.81, 116.63, 117.22, 123.47, 123.71, 123.92, 124.03, 125.12, 125.39, 125.54, 125.65, 141.77, 141.86, 142.02, 142.05, 155.23, 155.44, 155.60, 156.18, 181.14 (C=O). IR: 1652 (m, $\nu_{C=O}$), 1502 (w), 1295 (w), 1261 (sh), 1236 (s), 1171 (m), 1034 (m), 888 (w), 813 (w). UV-vis (toluene): 419 (2.0×10^4), 299 (5.9×10^4). FAB-MS: 917 (M+H$^+$). Anal. Calcd for $C_{51}H_{56}N_4O_9Ti$: C, 66.81; H, 6.16; N, 6.11. Found: C, 65.93; H, 5.97; N, 5.80.

[*N*,*N*′-Dimethyl-*N*,*N*′-bis-(2-oxido-5-(di-(4-methoxyphenyl)-amino)benzyl)ethylenediamine]-titanium(IV) dichloride, ^{An2N}LTiCl$_2$. ^{An2N}LTi(O^{i}Pr)$_2$ (0.1600 g, 0.174 mmol) was weighed into a 50 mL round-bottom flask with a stir bar and dissolved in CH_2Cl_2 (15 mL). To this solution, trimethylsilyl chloride (Aldrich, 0.0464 g, 0.427 mmol) in CH_2Cl_2 (5 mL) was added dropwise with vigorous stirring. The round-bottom flask was capped with

a needle valve and the reaction mixture stirred under nitrogen for 48 h. The volatiles were evaporated and the purple residue was allowed to stand under vacuum for 4 h. The flask was returned to the drybox and the solid dissolved in $CHCl_3$ (8 mL), layered with hexanes (5 mL) and Et_2O (5 mL), and stored at −35 °C. After 4 d, the supernatant was decanted and the dark purple solid vacuum dried for 30 min to give 0.1523 g (73%) of the dichloride complex. The analytical sample contained 0.5 mol CH_2Cl_2 and 0.5 mol hexane per mol complex. ^{1}H NMR ($CDCl_3$, added Cp*$_2$Fe): δ 2.28 (s, 3H, NCH_3), 2.31 (d, 12 Hz, 1H, NCH$_2$CHH′N), 2.41 (d, 12 Hz, 1H, NCHH′CH$_2$N), 3.12 (s, 3H, NCH_3), 3.19 (d, 13.5 Hz, 1H, NCHH′Ar), 3.36 (d, 15 Hz, 1H, NCHH′Ar), 3.68 (t, 11 Hz, 1H, NCH$_2$CHH′N), 3.78 (partially obscured t, 1H, NCHH′CH$_2$N) 3.79 (s, 6H, OCH_3), 3.80 (s, 6H, OCH_3), 5.00 (d, 14 Hz, 1H, NCHH′Ar), 5.29 (d, 13 Hz, 1H, NCHH′Ar), 6.51 (d, 8 Hz, 1H, Ar 3-H), 6.72 (m, 5H, ArH), 6.81 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 2,6-H), 6.83 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 2,6-H), 7.01 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H), 7.03 (d, 9 Hz, 4H, NC$_6$H$_4$OCH$_3$ 3,5-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 45.88 (NCH$_3$), 53.83 (NCH$_3$), 54.00 (NCH$_2$CH$_2$N), 55.71 (OCH$_3$), 58.12 (NCH$_2$$CH_2$N), 65.96 (N$CH_2$Ar), 66.22 (N$CH_2$Ar), 114.80, 114.91, 115.72, 116.37, 120.79, 121.54, 121.86, 122.04, 126.09, 126.15, 126.58, 128.23, 140.94, 141.36, 143.95, 144.43, 155.00, 155.71, 156.01, 156.03. IR: 1502 (s), 1484 (s), 1299 (w), 1267 (m), 1239 (s), 1183 (m), 1113 (w), 1088 (w), 1059 (w), 1043 (m), 888 (m), 825 (m), 780 (m), 706 (m), 678 (w). UV-vis: 543 (1.9×10^4), 298 (6.0×10^4). Anal. Calcd for $C_{49.5}H_{56}Cl_3N_4O_6Ti$: C, 62.11; H, 5.90; N, 5.85. Found: C, 61.57; H, 6.10; N, 5.95.

Electrochemistry

Electrochemical measurements were performed in the drybox using a BAS Epsilon potentiostat. A standard three-electrode setup was used, with a glassy carbon working electrode, Pt or glassy carbon counter electrode, and a silver/silver chloride pseudo-reference electrode. The electrodes were connected to the potentiostat through electrical conduits in the drybox wall. Samples were 1 mM in CH_2Cl_2, using 0.1 M Bu_4NPF_6 as the electrolyte. Potentials were referenced to ferrocene/ferrocenium at 0 V, with the reference potential established by spiking the test solution with a small amount of decamethylferrocene (E° = −0.565 V). Cyclic voltammograms were recorded with a scan rate of 60 mV s^{-1}. Square wave voltammograms were acquired with a step size of 3 mV, a pulse height of 30 mV, and a frequency of 15 Hz.

X-ray crystallography

Crystals of ^{An2N}LTi(O^{i}Pr)$_2$ were grown overnight from a solution in hexanes at room temperature. The crystals of ^{Br}LTi(OCH$_2$CMe$_2$COO)·0.5 HOCH$_2$CMe$_2$CO$_2$H·0.5 $CHCl_3$ were deposited on storage of the filtrate from the preparative procedure at −35 °C for 2 weeks. In each case, the crystal to be analyzed was placed in inert oil and transferred to a MiTeGen loop in the cold N_2 stream of a Bruker Apex CCD diffractometer. Data were corrected for absorption and polarization, and the space group was assigned using standard methods.[12] The structures were solved using direct methods, and all nonhydrogen atoms were treated anisotropically. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. Hydrogen atoms were placed in calculated positions, with thermal parameters for the hydrogens tied to the isotropic thermal parameter of the atom to which they are bonded (1.5× for methyl, 1.2× for all others). Calculations used SHELXTL (Bruker AXS),[13] with scattering factors and anomalous dispersion terms taken from the literature.[14] Further details about the structures are in Table 1.

Crystals of ^{An2N}LTi(OCMe$_2$CO$_2$) were deposited on standing of the mother liquor from its preparation. An arbitrary sphere

Table 1 X-ray crystallographic details for ^{An2N}LTi(O^{i}Pr)$_2$, ^{An2N}LTi(OCMe$_2$CO$_2$) and ^{Br}LTi(OCH$_2$CMe$_2$CO$_2$)·0.5 HOCH$_2$CMe$_2$CO$_2$H·0.5 $CHCl_3$

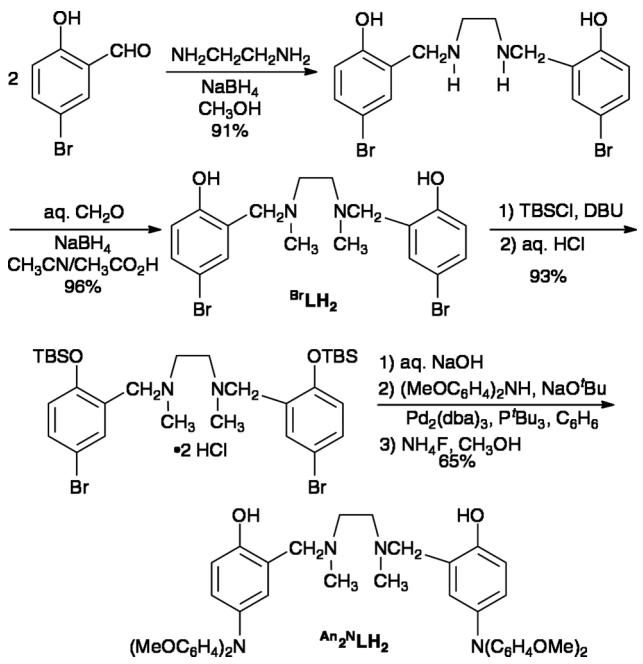
	^{An2N}LTi(O^{i}Pr)$_2$	^{An2N}LTi(OCMe$_2$CO$_2$)	^{Br}LTi(OCH$_2$CMe$_2$CO$_2$)·0.5 HOCH$_2$CMe$_2$CO$_2$H·0.5 $CHCl_3$
Molecular formula	$C_{52}H_{62}N_4O_8Ti$	$C_{50}H_{54}N_4O_9Ti$	$C_{26}H_{33.5}Br_2Cl_{1.5}N_2O_{6.5}Ti$
Formula weight	918.96	902.87	738.94
T/K	100(2)	150(2)	120(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
λ/Å	0.71073 (Mo-Kα)	0.7749 (synchrotron)	0.71073 (Mo-Kα)
Total data collected	34937	23821	87013
No. of indep reflns.	9682	8573	12258
R_{int}	0.0338	0.0845	0.0438
Obsd refls [$I > 2\sigma(I)$]	6830	4662	9986
a/Å	11.6904(6)	12.703(2)	19.9705(15)
b/Å	14.3149(8)	13.811(2)	21.2780(16)
c/Å	15.9465(8)	14.969(3)	14.1667(11)
α/°	66.280(2)	69.740(2)	90
β/°	87.702(2)	79.478(2)	98.6784(12)
γ/°	78.741(2)	73.082(2)	90
V/Å^3	2393.9(2)	2347.3(7)	5951.0(8)
Z	2	2	8
μ/mm^{-1}	0.237	0.266	3.152
Crystal size/mm	0.26 × 0.16 × 0.10	0.08 × 0.04 × 0.02	0.20 × 0.19 × 0.09
No. refined params	608	745	718
R_1, wR_2 [$I > 2\sigma(I)$]	0.0608, 0.1490	0.0552, 0.1142	0.0338, 0.0794

of data was collected at beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory on a red 0.08 × 0.04 × 0.02 mm plate on a Bruker APEX-II diffractometer using a combination of ω- and ϕ-scans of 0.3° at 150(2) K. Data were reduced and analyzed as described above. The titanium atom and the first coordination-sphere atoms were found using a Patterson map, with remaining heavy atoms found on subsequent difference Fourier syntheses. Hydrogen atoms were found on difference maps and refined isotropically, except for the hydrogens on the methoxy groups, which were placed in calculated positions.

Results and discussion

Synthesis of a diarylamino-substituted salan ligand

Preparation of the diarylamino-substituted salan ligand begins with commercially available 5-bromosalicylaldehyde. The tetrahydrosalen derivative of this aldehyde had previously been prepared in two steps, with isolation of the intermediate salen ligand;[11,15] we find that generation and *in situ* reduction of the salen ligand proceeds in excellent yield (Scheme 1). Methylation at nitrogen to prepare the bromosalan derivative $^{Br}LH_2$ is accomplished by reductive amination with formaldehyde as described by Walsh and coworkers for the 3,5-di-*tert*-butyl-substituted analogue.[16] This compound was previously prepared by Mannich condensation of *N*,*N*′-dimethylethylenediamine with 4-bromophenol in a single step, albeit in lower yield.[17]



Scheme 1 Synthesis of $^{An2N}LH_2$.

In the preparation of the redox-active tripodal ligands $N(CH_2C_6H_2\text{-}3\text{-}R\text{-}5\text{-}N(C_6H_4OMe)_2\text{-}2\text{-}OH)_3$ (R = H, ^{t}Bu), protection of the phenol group was required prior to reductive amination of the salicylaldehyde. A benzyl group was used to protect the starting salicylaldehyde, as has been done in other preparations of aminetrisphenolates,[18] even though deprotection was difficult in the *ortho*-substituted derivative. We had explored silyl protection of the salicylaldehyde, but found that silylation was incomplete and the resulting silyl compounds hydrolyzed readily. In contrast, in the preparation of the salan derivative, reductive amination proceeds even with the unprotected phenol, and silylation of the aminomethyl phenols is readily accomplished under standard conditions (*tert*-butyldimethylsilyl chloride, DBU). The free amine is an oil, but can be precipitated from dichloromethane as the dihydrochloride in pure form and in high yield. Neutralization of the hydrochloride salt, followed by palladium-catalyzed substitution of the aryl bromides with bis(4-methoxyphenyl)amine using Pd^0/P^tBu_3[19] gives the silyl-protected ligand. Desilylation of the crude material with ammonium fluoride in methanol produces the free ligand $^{An2N}LH_2$. The overall yield for the four-step synthesis is 53%, and each synthetic intermediate is isolated in pure form directly by precipitation, making this an efficient route to this electron-rich salan ligand.

Synthesis and structures of titanium(IV) salan complexes

Both $^{An2N}LH_2$ and its bromo analogue $^{Br}LH_2$ are rapidly metalated by titanium(IV) isopropoxide to give the corresponding $LTi(O^iPr)_2$ complexes (eqn (1)). *In situ* measurements indicate that the reactions are quantitative, and pure material can be isolated in high yield. NMR spectra indicate that these isopropoxide complexes exist as single geometric isomers with C_2 symmetry (*e.g.*, the benzylic methylene protons and the isopropoxide methyl groups are diastereotopic). The geometry is confirmed to be *cis*-α (rather than *trans*) by X-ray crystallography of $^{An2N}LTi(O^iPr)_2$ (Tables 1–2,

Table 2 Selected bond distances (Å) and angles (°) in $^{An2N}LTi(O^iPr)_2$, $^{An2N}LTi(OCMe_2CO_2)$ and $^{Br}LTi(OCH_2CMe_2CO_2)\cdot0.5\,HOCH_2CMe_2CO_2H\cdot0.5\,CHCl_3$

			$^{Br}LTi(OCH_2CMe_2CO_2)$[a]	
	$^{An2N}LTi(O^iPr)_2$	$^{An2N}LTi(OCMe_2CO_2)$	Molecule 1	Molecule 2
Ti–O1	1.916(2)	1.844(2)	1.851(2)	1.857(2)
Ti–O2	1.879(2)	1.842(2)	1.869(2)	1.851(2)
Ti–O3	1.813(2)	1.849(2)	1.809(2)	1.811(2)
Ti–O4	1.823(2)	1.999(2)	1.986(2)	1.982(2)
Ti–N1	2.332(2)	2.270(3)	2.274(2)	2.263(2)
Ti–N2	2.366(2)	2.295(3)	2.281(2)	2.299(2)
O1–Ti–O2	165.75(9)	100.15(10)	96.92(9)	95.55(8)
O1–Ti–O3	95.26(9)	105.34(11)	105.06(8)	102.81(8)
O1–Ti–O4	90.68(9)	93.03(10)	93.21(8)	94.79(8)
O1–Ti–N1	81.80(8)	82.25(10)	83.07(8)	83.85(8)
O1–Ti–N2	87.42(8)	159.38(10)	160.30(9)	161.24(8)
O2–Ti–O3	94.37(9)	96.66(10)	94.27(9)	98.54(9)
O2–Ti–O4	96.51(9)	166.79(10)	169.03(8)	167.22(8)
O2–Ti–N1	88.03(8)	96.12(10)	92.00(9)	92.36(8)
O2–Ti–N2	80.32(8)	82.66(10)	83.69(8)	82.87(8)
O3–Ti–O4	107.03(10)	80.57(10)	87.14(8)	86.44(8)
O3–Ti–N1	88.25(9)	163.70(10)	169.02(9)	166.54(9)
O3–Ti–N2	162.68(9)	94.52(11)	94.50(9)	95.90(8)
O4–Ti–N1	163.59(9)	84.69(10)	85.02(8)	81.30(8)
O4–Ti–N2	90.01(9)	84.67(9)	85.35(8)	84.92(8)
N1–Ti–N2	75.16(8)	77.14(10)	77.23(8)	77.56(8)
Ti–O1–C11	139.82(18)	138.4(2)	140.2(2)	139.9(2)
Ti–O2–C21	142.45(17)	142.9(2)	141.0(2)	144.1(2)
Ti–O3–C*x*	141.7(3)[b]	120.6(2)[c]	134.7(2)[d]	135.0(2)[d]
Ti–O4–C*y*	140.9(2)[b]	116.6(2)[c]	133.1(2)[d]	133.6(2)[d]

[a] Numbers in atom labels for each independent molecule are preceded by the molecule number (*e.g.*, C11 in molecule 2 is C211). [b] $x = 6A$, $y = 9$. [c] $x = 5$, $y = 6$. [d] $x = 5$, $y = 7$.

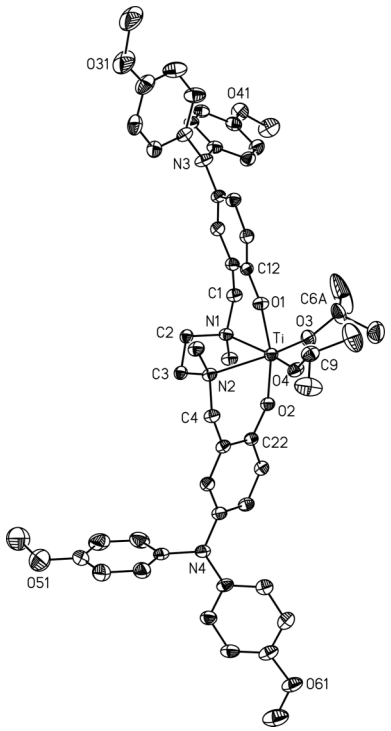
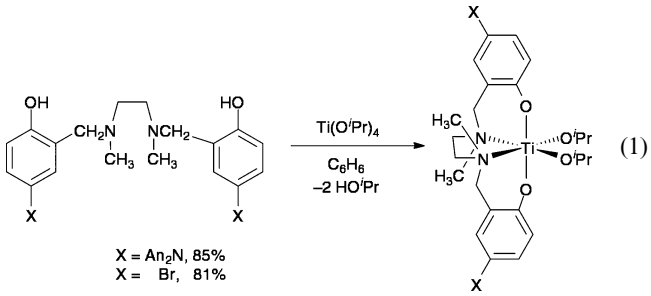


Fig. 1 Thermal ellipsoid plot of ^{An2N}LTi(O^{i}Pr)$_2$, with hydrogen atoms omitted for clarity. Only the major orientation of the isopropyl group bonded to O3 is shown.

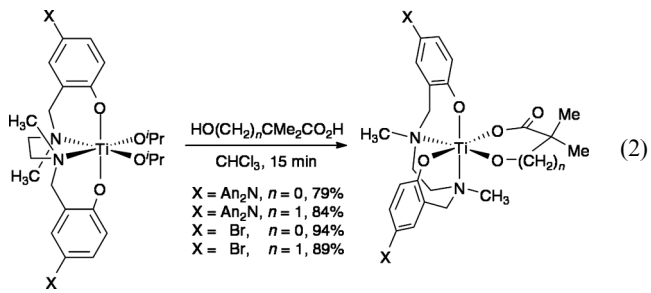
Fig. 1). This geometry is hardly surprising, since a large number of (salan)titanium(IV) dialkoxides with varying substituents on the nitrogens and aryl rings have been prepared, and structurally characterized examples are *cis*-α[6c,16,20,21] with only a single exception. (The parent salan complex (salan)Ti(O^{i}Pr)$_2$ is *cis*-β in the solid state, though it appears to be *cis*-α in solution.[22]) Bond distances and angles in the diarylamino-substituted complex described here are fairly typical. For example, while one of the aryloxide-titanium distances (Ti–O2, 1.879(2) Å) is (barely) outside of the range observed to date (1.884–1.967 Å in 44 examples), the chemically (but not crystallographically) equivalent distance (Ti–O1, 1.916(2) Å) is quite typical (literature average 1.92(2) Å). Thus, on average, the aryloxide–Ti distances in ^{An2N}LTi(O^{i}Pr)$_2$ are at the low end of, but well within, the observed range. The triarylamine fragment is essentially planar at nitrogen (sum of angles = 358.8° and 358.9° at N3 and N4, respectively), with the three aryl rings forming a propeller shape (angles with the NC$_3$ planes of 46(16)°). These features are typical of neutral triarylamines.[23]

We have previously used the formation of titanium chelates of ω-hydroxycarboxylic acids as a way of probing the effects of ancillary ligation with two groups of dissimilar *trans* influence.[24] The titanium isopropoxide complexes LTi(O^{i}Pr)$_2$ react rapidly with α-hydroxyisobutyric acid or 2,2-dimethyl-3-hydroxypropanoic acid (hydroxypivalic acid) to form chelated alkoxy-carboxylates with 5- or 6-membered chelate rings, respectively (eqn (2)). NMR spectra of the bromo-substituted and diarylamino-substituted salan complexes are very similar to each other, and in each of the four compounds only one C_1-symmetric isomer is apparent by NMR.



(1)

Crystallography of ^{An2N}LTi(OCMe$_2$CO$_2$) and ^{Br}LTi(OCH$_2$CMe$_2$CO$_2$) (Fig. 2–3) indicates that the geometry of these compounds is *cis*-β, with the alkoxide group of the alkoxy-carboxylate *trans* to one of the amine nitrogens while the other amine is *trans* to one of the aryloxide groups. (The latter compound cocrystallizes with a disordered molecule of hydroxypivalic acid linking two complexes in the asymmetric unit by hydrogen bonding to the carbonyl oxygens of the bound hydroxypivalates.) The *cis*-β geometry is less commonly observed in titanium salan complexes than the *cis*-α geometry, but has been previously seen in catecholate[21a] and μ-oxo complexes.[7,20] Replacement of an alkoxide with a carboxylate renders the titanium centres more electron-deficient, as judged by the contraction of the titanium–aryloxide and titanium–amine bonds by ~0.05 Å and ~0.07 Å, respectively, compared to the diisopropoxide complex. The five-membered chelate ring size has a noticeable effect on the bonding of the alkoxide group to titanium. While the alkoxides normally form the shortest bonds to Ti (1.818(7) Å avg. in ^{An2N}LTi(O^{i}Pr)$_2$ and 1.810(2) Å avg. in ^{Br}LTi(OCH$_2$CMe$_2$CO$_2$)), the Ti–alkoxide bond in ^{An2N}LTi(OCMe$_2$CO$_2$) is appreciably longer (1.849(2) Å) and is actually slightly longer than the Ti–aryloxide bonds in that complex. The small ring imposes a relatively acute Ti–O–C angle (120.6(2)°, compared to 135–142° observed in the other alkoxides), which likely diminishes its Ti–O π interactions.[25,26] The half-chair conformation of the six-membered hydroxypivalate ring has been observed previously in titanium complexes.



(2)

The dark purple dichloride complex ^{An2N}LTiCl$_2$ can be prepared by reaction of the corresponding diisopropoxide complex with Me$_3$SiCl (eqn (3)), a procedure which has also been used to prepare bis(diketonato)titanium(IV) dichlorides.[9,27] The monochloro complex ^{An2N}LTi(O^{i}Pr)Cl can be observed as an intermediate in this reaction by *in situ* NMR monitoring. NMR resonances for the isolated dichloride complex are broadened due to partial oxidation of the triarylamine groups. Addition of traces of decamethylferrocene (to fully reduce any radical cations) causes the spectra to sharpen, showing that a single, C_1-symmetric isomer is present in solution. Based on its low symmetry and the similarity

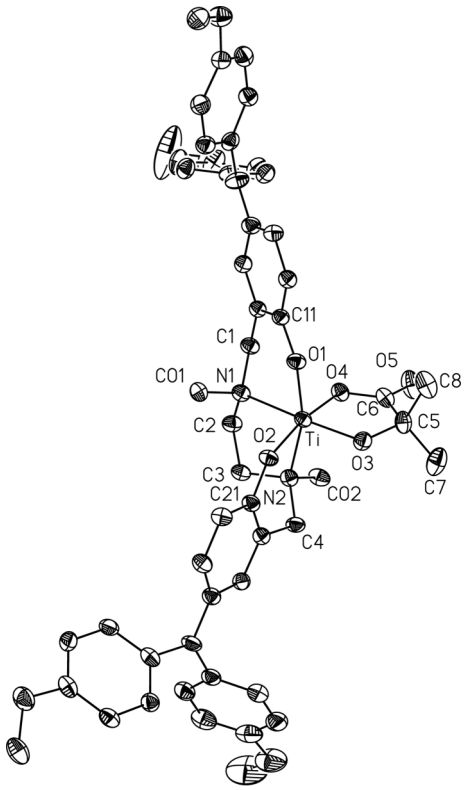


Fig. 2 Thermal ellipsoid plot of ^{An2N}LTi(OCMe$_2$CO$_2$), with hydrogen atoms omitted for clarity.

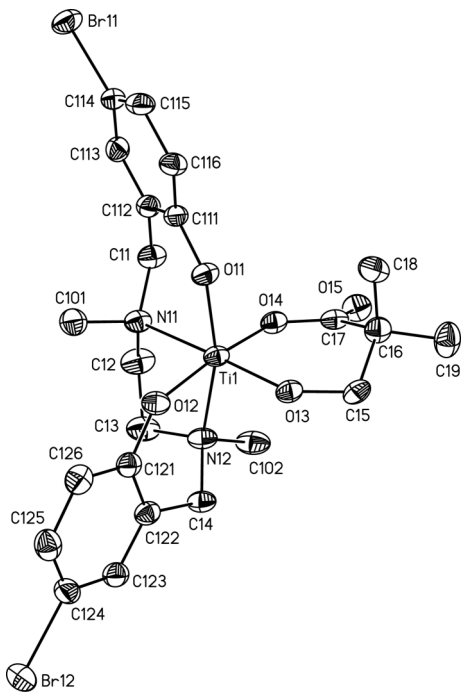
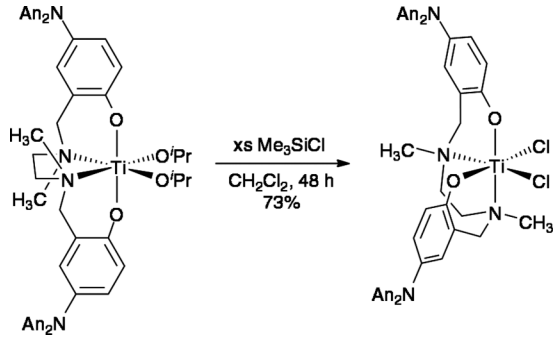


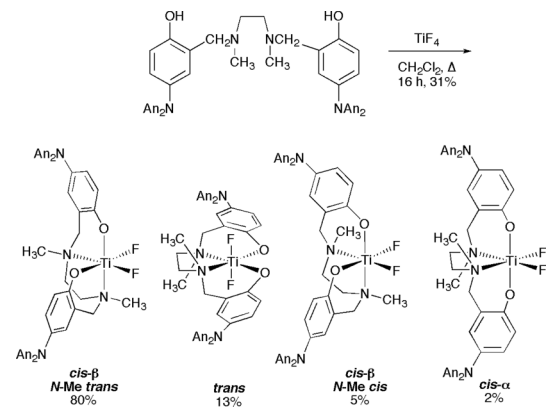
Fig. 3 Thermal ellipsoid plot of one of the crystallographically inequivalent titanium complexes in ^{Br}LTi(OCH$_2$CMe$_2$CO$_2$)·0.5 HOCH$_2$CMe$_2$CO$_2$H·0.5 CHCl$_3$, with hydrogen atoms omitted for clarity.

of the ^{1}H NMR spectra to those of the alkoxy-carboxylates, the compound is assigned as the *cis*-β isomer.



(3)

Attempts to prepare the corresponding fluoro complex by ligand replacement reactions of ^{An2N}LTi(O^{i}Pr)$_2$ with, *e.g.*, ammonium fluoride, were not successful. The fluoride complex could be prepared in moderate yield by metalation of the free ligand with titanium(IV) fluoride (eqn (4)). As judged by ^{1}H and ^{19}F NMR spectroscopy (Fig. 4), ^{An2N}LTiF$_2$ exists as a mixture of isomers. The major isomer, accounting for 80% of the material, is assigned as the *cis*-β isomer on the basis of the similarity of its ^{1}H NMR spectrum to those of the other *cis*-β compounds. It displays two doublets with a coupling constant J_{FF} = 40 Hz typical of *cis*-TiF$_2$ units[28] in its ^{19}F NMR spectrum, consistent with inequivalent fluorine environments. Based on the firmly established observation that fluorines *trans* to fluorine resonate substantially upfield of fluorines *trans* to neutral donors in L$_2$TiF$_4$ and [LTiF$_5$]$^-$ complexes,[29,30] the upfield resonance (δ 100.1) is assigned to the fluorine *trans* to aryloxide and the downfield resonance (δ 146.4) to the fluorine *trans* to nitrogen. A smaller pair of doublets (5% of the total intensity) with similar chemical shifts and coupling constant (J_{FF} = 36 Hz) to those of the major isomer are also assigned as originating from a *cis*-β isomer, differing from the major isomer in the stereochemistry of the ethylenediamine ring by having the nitrogen substituents *cis* rather than *trans*. This arrangement of nitrogen substituents is much rarer than the *trans* arrangement but has been observed in two di-μ-oxodititanium salan complexes.[7b]



(4)

Two other singlets of unequal intensity, therefore attributed to two different symmetrical difluoride complexes, are also observed in the ^{19}F NMR. The only possible isomers with equivalent fluorine environments are the *cis*-α and the *trans* isomer. Based on the chemical shifts, the upfield signal (13%) is assigned to the *trans* isomer (F atoms mutually *trans*) and the downfield signal (2%) to the *cis*-α isomer (F *trans* to N). While the *trans* isomer has not been previously observed in a simple salan ligand bonded to

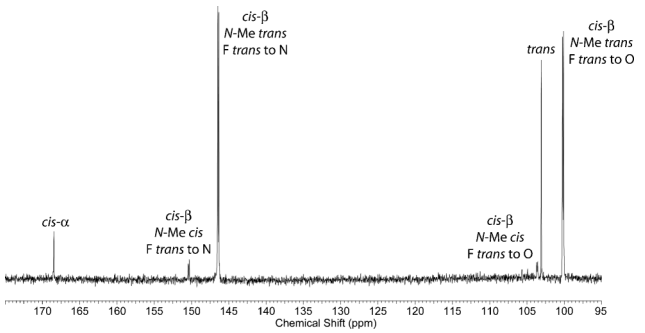


Fig. 4 ^{19}F NMR spectrum of $^{An2N}LTiF_2$ (CD_2Cl_2, chemical shifts in ppm downfield of $CFCl_3$). The spectrum was taken in the presence of traces of decamethylferrocene to reduce adventitiously oxidized triarylamines.

titanium, it is certainly geometrically accessible for the ligand, as witnessed by numerous late metal salan complexes with this configuration and by structures of salan-like hexadentate ligands bonded to titanium.[31]

A superficial examination of the literature of (salan)Ti(IV) complexes might lead to the conclusion that the C_2-symmetric *cis*-α configuration is strongly preferred by this ligand, and indeed this observation has been adduced as the basis for examining these ligands for preparing isospecific Ziegler–Natta polymerization catalysts.[32] The complexes prepared here suggest that the preponderance of the *cis*-α configuration observed in the literature is not a reflection of the intrinsic geometric predilection of the salan ligand but rather an artifact of the predominance of dialkoxide complexes in the literature. Rather than depending primarily on the salan ligand, the observed geometric preferences in solution can be best rationalized as reflecting the competing *trans* influences of the amine, aryloxide, and other ligands at titanium. Because alkoxide ligands are more strongly donating than aryloxides, they prefer to be *trans* to the weakly donating amine ligands, giving *cis*-α complexes. When one alkoxide is replaced by a carboxylate, the aryloxide has the second-strongest *trans* influence in the complex, and so the *cis*-β geometry, which allows the alkoxide and one aryloxide to be *trans* to the amines, is adopted. The preference of the dichloride complex to be *cis*-β can be rationalized if the *trans* influence of chloride is even lower than that of amine, as this geometry allows one aryloxide to be *trans* to chloride (and no geometry would allow both to be *trans* to chloride). Finally, the structural diversity exhibited by $^{An2N}LTiF_2$ emphasizes the intrinsic flexibility of the salan ligand itself and is consistent with fluoride having a rather similar *trans* influence to aryloxide, rendering all geometries electronically quite similar. While fluoride is a weaker Brønsted base than aryloxide, titanium is more electropositive than hydrogen and is thus expected to form a relatively stronger bond to fluorine; note that typical Ti–F distances in neutral octahedral titanium(IV) fluorides (1.75–1.82 Å)[33] are similar to the bond lengths in titanium aryloxides.

From the structural trends observed in these complexes, one may thus infer a ladder of *trans* influences of OR > OAr ≈ F > O_2CR > NR_3 > Cl. The *trans* influence is known to be important in determining the geometry of titanium(IV) complexes,[34] and the ordering seen here is mostly in agreement with previous studies. The exception is that chloride usually appears to exert a stronger *trans* influence than neutral nitrogen donors. For example, (2,6-$Me_2C_6H_3O)_2TiCl_2$(diamine)[35] and (TADDOL)$TiCl_2$(bpy)[36] have the aryloxide or alkoxide ligands *trans* to nitrogen, not chloride. In the salan complex, the *trans* isomer (which would allow both aryloxides to be *trans* to nitrogen) may be disfavored by the relatively obtuse O–Ti–O angle (~110°) imposed by geometrical constraints of the chelate. A wide angle diminishes the ability of the aryloxide ligands to donate to the *B*-symmetry dπ orbital and would thus decrease the stability of the *trans* isomer. This effect would be much less important in the difluoride complex (which is 13% *trans*) because of the greater ability of fluoride compared to chloride to donate to this dπ orbital.

The geometric flexibility of the salan ligand may have implications in the reactivity of its complexes. For example, abstraction of a methyl group from a *cis*-α (salan)$ZrMe_2$ complex leads to rearrangement to form a compound assigned on the basis of NMR and DFT evidence to a square pyramidal geometry with the methyl group apical (*i.e.*, *trans* to the vacant coordination site) and the salan ligand adopting a *trans* geometry.[37] Thus, while the neutral compound is geometrically similar to a C_2-symmetric dialkylzirconocene, the cationic species involved in olefin polymerization differs dramatically in its stereochemistry, with implications for both reactivity and stereoselectivity in enchainment.

Optical and electrochemical properties of diarylamino-substituted (salan)titanium complexes

The UV-visible spectra of $^{An2N}LTi(X)(Y)$ complexes show, in addition to a very intense ligand-centered π–π* transition at 300 nm, ligand-to-metal charge transfer transitions at longer wavelengths (Fig. 5). As expected for a LMCT transition, the absorption feature moves to lower energy as the titanium becomes more electron-poor, with λ_{max} shifting from 365 nm for the diisopropoxide to 543 nm for the dichloride. The alkoxy-carboxylate complexes show peaks at intermediate wavelengths. The difluoride complex shows an optical spectrum that is very similar to those of the alkoxy-carboxylates, suggesting that fluoride is intermediate in its

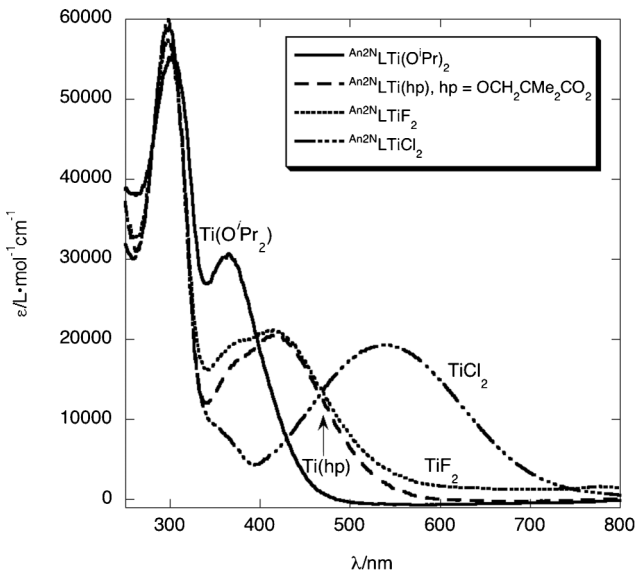


Fig. 5 UV-visible spectra (CH_2Cl_2) of $^{An2N}LTi(O^iPr)_2$ (solid line), $^{An2N}LTi(OCH_2CMe_2CO_2)$ (dashed line), $^{An2N}LTiF_2$ (dotted line) and $^{An2N}LTiCl_2$ (dot-dash line).

Table 3 Redox potentials for triarylamine oxidation in ^{An2N}LTi complexes (CH_2Cl_2, 0.1 M Bu_4NPF_6, V *vs.* Cp_2Fe^+/Cp_2Fe)

Complex	E°_1	E°_2	E°_3	E°_4
^{An2N}LTi($OCMe_2CO_2$)	0.059	0.147	0.739	0.875
^{An2N}LTi($OCH_2CMe_2CO_2$)	0.059	0.119	0.715	0.843
^{An2N}LTiF_2	0.063	0.143	0.719	0.887

donor ability between alkoxide and carboxylate, consistent with its position in the *trans* influence series described above.

Para-trisubstituted triarylamines typically show reversible electrochemistry, and electron-rich triarylamines often show two reversible oxidations, one from the neutral species to the radical cation, and a subsequent oxidation of the radical cation to form a quinonoid dication.[38] This pattern is observed in most of the ^{An2N}LTi complexes (*e.g.*, Fig. 6), where two closely spaced oxidations are observed at ~ +0.1 V (*vs.* Cp_2Fe^+/Cp_2Fe) and a second set of closely spaced oxidations are observed at ~ +0.8 V (Table 3). The Ti(IV)/Ti(III) reduction can also be observed, at very negative potentials (~ −2 V). These potentials, as well as the 50–100 mV separation between the oxidation waves, are similar to those previously observed in tripodal (N[$CH_2C_6H_3$-5-NAn_2-2-O]$_3$)TiX complexes. The bromosalan complexes show no oxidations at potentials below 1 V.

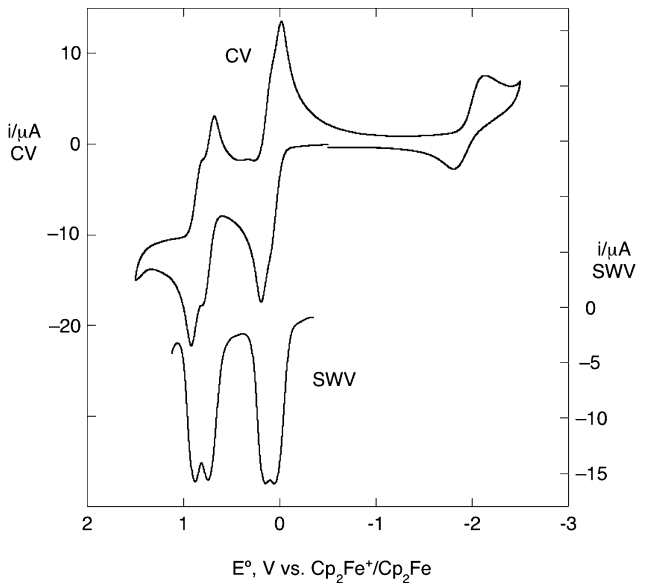


Fig. 6 Electrochemistry of ^{An2N}LTi($OCMe_2CO_2$) in CH_2Cl_2 (1 mM, 0.1 M Bu_4NPF_6 electrolyte). Top trace, left axis: cyclic voltammogram (60 mV s^{-1}). Bottom trace, right axis: square wave voltammogram.

An exception to the general trend of reversible oxidation of the triarylamine moieties is ^{An2N}LTi(O^iPr)$_2$, which shows only a single, irreversible oxidation wave between 0–1 V. The irreversibility is not due to gross decomposition of the oxidized product, as chemical oxidation using ferrocenium hexafluorophosphate to give a dark green solution of oxidized material, followed by reduction with cobaltocene, leads to a 68% recovery of isopropoxide complex (measured by ^{1}H NMR integration *vs.* an internal standard) even after 1 h standing of the oxidized material.

Conclusions

A *para*-diarylamino-substituted salan ligand is readily prepared in four steps from 5-bromosalicylaldehyde in 53% overall yield. It, like the bromosalan analogue, readily forms complexes of titanium(IV) with a variety of chelating and monodentate ancillary ligands. The intrinsic geometrical preferences of the salan backbone appear to be small, with the observed geometry governed mainly by the *trans* influence of the ancillary groups. Each diarylaminoaryloxide group usually undergoes two pairs of reversible oxidations, at ~0.1 V and ~0.8 V, with modest (50–150 mV) separations between the redox potentials of the two arms of the salan ligand. The ability of these ligands to reversibly store oxidizing equivalents will be explored as a way to mediate redox reactions at the titanium(IV) centre.

Acknowledgements

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. A. J. L. thanks the U. S. National Science Foundation (CHE-0518243) for summer support. The sample of ^{An2N}LTi($OCMe_2CO_2$) was submitted for synchrotron crystallographic analysis through the SCrALS (Service Crystallography at Advanced Light Source) program. Crystallographic data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the U.S. Dept. of Energy, Office of Energy Sciences, under contract DE-AC02-05CH11231.

References

1 (*a*) L. Canali and D. C. Sherrington, *Chem. Soc. Rev.*, 1999, **28**, 85–93; (*b*) T. Katsuki, *Adv. Synth. Catal.*, 2002, **344**, 131–147; (*c*) P. G. Cozzi, *Chem. Soc. Rev.*, 2004, **33**, 410–421; (*d*) S. J. Wezenberg and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2008, **47**, 2354–2364.
2 (*a*) Y. Shimazaki, F. Tani, K. Fukui, Y. Naruta and O. Yamauchi, *J. Am. Chem. Soc.*, 2003, **125**, 10512–10513; (*b*) O. Rotthaus, F. Thomas, O. Jarjayes, C. Philouze, E. Saint-Aman and J.-L. Pierre, *Chem.–Eur. J.*, 2006, **12**, 6953–6962; (*c*) Y. Shimazaki, T. Yajima, F. Tani, S. Karasawa, K. Fukui, Y. Naruta and O. Yamauchi, *J. Am. Chem. Soc.*, 2007, **129**, 2559–2568; (*d*) T. Storr, E. C. Wasinger, R. C. Pratt and T. D. P. Stack, *Angew. Chem., Int. Ed.*, 2007, **46**, 5198–5201; (*e*) T. Storr, P. Verma, R. C. Pratt, E. C. Wasinger, Y. Shimazaki and T. D. P. Stack, *J. Am. Chem. Soc.*, 2008, **130**, 15448–15459; (*f*) Y. Shimazaki, T. D. P. Stack and T. Storr, *Inorg. Chem.*, 2009, **48**, 8383–8392; (*g*) E. Deunf, E. Zaborova, S. Guieu, Y. Bleriot, J.-N. Verpeaux, O. Buriez, M. Sollogoub and C. Amatore, *Eur. J. Inorg. Chem.*, 2010, 4720–4727; (*h*) F. Thomas, H. Arora, C. Philouze and O. Jarjayes, *Inorg. Chim. Acta*, 2010, **363**, 3122–3130.
3 O. Rotthaus, O. Jarjayes, C. P. Del Valle, C. Philouze and F. Thomas, *Chem. Commun.*, 2007, 4462–4464.
4 (*a*) H.-J. Krüger, *Angew. Chem., Int. Ed.*, 1999, **38**, 627–631; (*b*) B. A. Jazdzewski and W. B. Tolman, *Coord. Chem. Rev.*, 2000, **200**, 633–685; (*c*) V. Mahadevan, R. J. M. Klein Gebbink and T. D. P. Stack, *Curr. Opin. Chem. Biol.*, 2000, **4**, 228–234.
5 (*a*) B. Adam, E. Bill, E. Bothe, B. Goerdt, G. Haselhorst, K. Hildenbrand, A. Sokolowski, S. Steenken, T. Weyhermüller and K. Wieghardt, *Chem.–Eur. J.*, 1997, **3**, 308–319; (*b*) P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 2001, **50**, 151–216.
6 (*a*) K. Matsumoto, Y. Sawada, B. Saito, K. Sakai and T. Katsuki, *Angew. Chem., Int. Ed.*, 2005, **44**, 4935–4939; (*b*) M. K. Panda, M. M. Shaikh and P. Ghosh, *Dalton Trans.*, 2010, **39**, 2428–2440.
7 (*a*) Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito and T. Katsuki, *Angew. Chem., Int. Ed.*, 2006, **45**, 3478–3480; (*b*) S. Kondo, K. Saruhashi, K. Seki, K. Matsubara, K.

Miyaji, T. Kubo, K. Matsumoto and T. Katsuki, *Angew. Chem., Int. Ed.*, 2008, **47**, 10195–10198.
8 C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford and A. J. P. White, *J. Am. Chem. Soc.*, 2006, **128**, 7410–7411.
9 L. T. Dulatas, S. N. Brown, E. Ojomo, B. C. Noll, M. J. Cavo, P. B. Holt and M. M. Wopperer, *Inorg. Chem.*, 2009, **48**, 10789–10799.
10 D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2010, **49**, 4687–4697.
11 C. Spanka, P. Buhlmayer. *PCT Int. Appl.* 1997, WO 9744313.
12 *Bruker AXS, APEX2 and SAINT*, 2008, Bruker-Nonius AXS, Madison, Wisconsin, USA.
13 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112–122.
14 *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Vol C.
15 (*a*) E. Wong, S. Liu, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 1995, **34**, 3057–3064; (*b*) M. Lanznaster, A. Neves, A. J. Bortoluzzi, A. M. C. Assumpção, I. Vencato, S. P. Machado and S. M. Drechsel, *Inorg. Chem.*, 2006, **45**, 1005–1011.
16 J. Balsells, P. J. Carroll and P. J. Walsh, *Inorg. Chem.*, 2001, **40**, 5568–5574.
17 C. J. Whiteoak, G. J. P. Britovsek, V. C. Gibson and A. J. P. White, *Dalton Trans.*, 2009, 2337–2344.
18 (*a*) L. J. Prins, M. M. Blázquez, A. Kolarović and G. Licini, *Tetrahedron Lett.*, 2006, **47**, 2735–2738; (*b*) P. Axe, S. D. Bull, M. G. Davidson, C. J. Gilfillan, M. D. Jones, D. E. J. E. Robinson, L. E. Turner and W. L. Mitchell, *Org. Lett.*, 2007, **9**, 223–226; (*c*) G. Bernardinelli, T. M. Seidel, E. P. Kündig, L. J. Prins, A. Kolarovic, M. Mba, M. Pontini and G. Licini, *Dalton Trans.*, 2007, 1573–1576.
19 J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy and L. M. Alcazar-Roman, *J. Org. Chem.*, 1999, **64**, 5575–5580.
20 (*a*) S. Segal, I. Goldberg and M. Kol, *Organometallics*, 2005, **24**, 200–202; (*b*) A. Yeori, S. Groysman, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, **44**, 4466–4468; (*c*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. J. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257; (*d*) M. Shavit, D. Peri, C. M. Manna, J. S. Alexander and E. Y. Tshuva, *J. Am. Chem. Soc.*, 2007, **129**, 12098–12099; (*e*) T. A. Immel, M. Debiak, U. Groth, A. Burkle and T. Huhn, *ChemMedChem*, 2009, **4**, 738–741; (*f*) S. N. MacMillan, C. F. Jung, T. Shalumova and J. M. Tanski, *Inorg. Chim. Acta*, 2009, **362**, 3134–3146; (*g*) S. H. Kim, J. Lee, D. J. Kim, J. H. Moon, S. Yoon, H. J. Oh, Y. Do, Y. S. Ko, J.-H. Yim and Y. Kim, *J. Organomet. Chem.*, 2009, **694**, 3409–3417; (*h*) C. M. Manna and E. Y. Tshuva, *Dalton Trans.*, 2010, **39**, 1182–1184; (*i*) M. K. Panda, S. Kaur, A. R. Reddy, M. M. Shaikh, R. J. Butcher, V. Gupta and P. Ghosh, *Dalton Trans.*, 2010, **39**, 11060–11068; (*j*) T. A. Immel, U. Groth and T. Huhn, *Chem.–Eur. J.*, 2010, **16**, 2775–2789.
21 (*a*) D. Peri, S. Meker, M. Shavit and E. Y. Tshuva, *Chem.–Eur. J.*, 2009, **15**, 2403–2415; (*b*) D. Peri, S. Meker, C. M. Manna and E. Y. Tshuva, *Inorg. Chem.*, 2011, **50**, 1030–1038.
22 M. D. Jones, M. G. Davidson and G. Kociok-Kohn, *Polyhedron*, 2010, **29**, 697–700.
23 M. Quiroz-Guzman and S. N. Brown, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2010, **C66**, m171–m173.
24 N. Kongprakaiwoot, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2008, **47**, 11902–11909.
25 G. D. Smith, P. E. Fanwick and I. P. Rothwell, *Inorg. Chem.*, 1990, **29**, 3221–3226.
26 A. G. Maestri and S. N. Brown, *Inorg. Chem.*, 2004, **43**, 6995–7004.
27 V. Ugrinova, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2006, **45**, 10309–10320.
28 M. Jura, W. Levason, E. Petts, G. Reid, M. Webster and W. Zhang, *Dalton Trans.*, 2010, **39**, 10264–10271.
29 (*a*) D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, 1967, **6**, 8–11; (*b*) T. S. Cameron, A. Decken, E. G. Ilyin, G. B. Nikiforov and J. Passmore, *Eur. J. Inorg. Chem.*, 2004, 3865–3872.
30 H. G. Lee, D. S. Dyer and R. O. Ragsdale, *J. Chem. Soc., Dalton Trans.*, 1976, 1325–1329.
31 (*a*) H. Hefele, E. Ludwig, W. Bansse, E. Uhlemann, T. Lügger, E. Hahn and H. Mehner, *Z. Anorg. Allg. Chem.*, 1995, **621**, 671–674; (*b*) A. D. Tinoco, C. D. Incarvito and A. M. Valentine, *J. Am. Chem. Soc.*, 2007, **129**, 3444–3454; (*c*) T. J. Boyle, H. D. Pratt, L. A. M. Ottley, T. M. Alam, S. K. McIntyre, M. A. Rodriguez, J. Farrell and C. F. Campana, *Inorg. Chem.*, 2009, **48**, 9191–9204.
32 (*a*) A. Yeori, I. Goldberg, M. Schuster and M. Kol, *J. Am. Chem. Soc.*, 2006, **128**, 13062–13063; (*b*) E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Chem. Commun.*, 2009, 3053–3055.
33 A. Decken, E. G. Ilyin, H. D. B. Jenkins, G. B. Nikiforov and J. Passmore, *Dalton Trans.*, 2005, 3039–3050.
34 H.-M. Gau, C.-S. Lee, C.-C. Lin, M.-K. Jiang, Y.-C. Ho and C.-N. Kuo, *J. Am. Chem. Soc.*, 1996, **118**, 2936–2941.
35 A. O. Larsen, P. S. White and M. R. Gagné, *Inorg. Chem.*, 1999, **38**, 4824–4828.
36 W.-S. Sheen and H.-M. Gau, *Inorg. Chim. Acta*, 2004, **357**, 2279–2284.
37 G. Ciancaleoni, N. Fraldi, P. H. M. Budzelaar, V. Busico and A. Macchioni, *Dalton Trans.*, 2009, 8824–8827.
38 S. Amthor, B. Noller and C. Lambert, *Chem. Phys.*, 2005, **316**, 141–152.

