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Chiral N_2O_2 Schiff-base complexes of titanium with a biaryl backbone: highly diastereoselective migratory insertion of alkyl at imine

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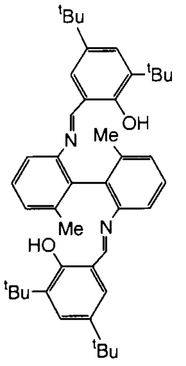
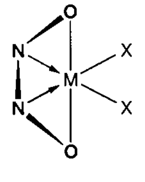
The C_2-symmetric Schiff-base proligand (H_2L) synthesized by condensation of 2,2′-diamino-6,6′-dimethylbiphenyl and 3,5-di-*tert*-butylsalicylaldehyde reacted in its deprotonated form with TiX_4 (X = Cl or Br) to give the isomeric mixtures α-*cis*- and β-*cis*-[MLX_2]. The molecular structure of α-*cis*-[$TiLBr_2$] was determined. The two bromide ligands occupy mutually *cis* co-ordination sites in a C_2-symmetric structure. Reaction of the isomeric mixture X = Cl with $LiNMe_2$ leads to the single isomer α-*cis*-[$TiL(NMe_2)_2$] as determined by NMR spectroscopy. Reaction of the latter complex with BCl_3 reconverts it into the chloride complex in a similar isomeric mixture as above. While attempts to alkylate the halides were unsuccessful, the reaction of H_2L with [$Ti(CH_2Ph)_4$] leads to α-*cis*-[$TiL(CH_2Ph)_2$] which rapidly converts into a complex [$TiL^{Bn}(CH_2Ph)$] in which one of the Ti bound benzyl groups has undergone a highly diastereoselective 1,2-migratory insertion process with one imine group. The molecular structure of this compound shows that the co-ordination sphere of the Ti atom is approximately trigonal bipyramidal. The configuration of the new chiral centre at the former imine group indicates the expected mode of *cis* migration in the formation of the complex. The migrated benzyl group forms an edge–face interaction with the remaining metal bound benzyl. Controlled hydrolysis of [$TiL^{Bn}(CH_2Ph)$] leads to a dimeric species [$\{Ti(HL^{Bn})\}_2$-(μ-O)$_2$] in which the amide bond in the starting complex has been protonated to form an amine ligand.

Introduction

We have described the synthesis of Schiff base proligands H_2L based on 2,2′-diamino-6,6′-dimethylbiphenyl and the synthesis of a range of zirconium complexes [$ZrLX_2$].[1,2] The most important feature of these compounds is that the co-ligands (*e.g.* halide, amide and alkoxide) occupy mutually *cis* co-ordination sites in a C_2-symmetric complex, *i.e.* the α-*cis* isomers are formed. This is quite unlike the behaviour of systems incorporating salen type ligands in which the co-ligands are invariably mutually *trans*.



H_2L



α-*cis*-[MLX_2]

We reported that the dialkyl complexes of this system, *i.e.* X = R, formed by reaction of H_2L with ZrR_4, were unstable and that the reaction of [$ZrLCl_2$] with a range of alkylating agents was unsuccessful. We conjectured that inter- or intra-molecular addition of alkyl groups at the activated imine groups was taking place, and indeed such behaviour is well documented in Schiff base chemistry of the early transition metals (see below). We have also characterised a related intermolecular diastereoselective radical addition chemistry in niobium systems.[3] The synthesis of alkyl complexes of titanium supported by Schiff-base ligature is more readily achieved however[4,5] and we thus set out to investigate whether complexes of the type [$TiLR_2$] could be isolated. In this paper we describe the synthesis and structural properties of titanium complexes based on L, and the instability of the dibenzyl derivative with respect to diastereoselective 1,2-migratory insertion at one ligand N=C group.

Experimental

General

Unless otherwise stated, all manipulations were carried out under an atmosphere of dry argon using conventional Schlenk techniques and a MBraun glove box operating at <0.5 ppm of O_2/H_2O. All solvents were dried by refluxing for three days over an appropriate agent (sodium for toluene; potassium for THF and benzene; sodium–potassium alloy for diethyl ether, light petroleum, and pentane; calcium hydride for dichloromethane and pyridine). Deuteriated solvents were heated to a few °C below their normal boiling points *in vacuo* over the appropriate agent (as above) before trap-to-trap distillation and storage in the glove box. NMR samples were made up in the glove box in tubes sealed with Young's concentric stopcocks.

NMR spectra were recorded on Bruker AC-250, AC-400 or DMX-300 spectrometers and referenced internally using residual protio solvent resonances relative to tetramethylsilane (δ 0), infrared spectra as Nujol mulls in an air tight holder on a Perkin-Elmer FT-IR spectrometer and EI mass spectra on a VG Autospec mass spectrometer by Dr Ali Abdul-Sada at the University of Sussex. Elemental analyses were performed by

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Canadian Microanalytical Services Ltd or Warwick Analytical Services.

The compounds $LiNMe_2$ and BCl_3 were purchased from Aldrich Chemical Company and used as supplied.

Syntheses

$[TiLCl_2]$ 1. *Method A.* A solution of $[Na_2(THF)_n][L]^2$ (2.00 g, 2.51 mmol) in diethyl ether (10 ml) was added dropwise to titanium tetrachloride (476 mg, 2.51 mmol) in diethyl ether (10 ml). The mixture rapidly turned dark red, and was stirred for 16 h. Volatile components were removed under reduced pressure and the solid residue was transferred to a sublimation tube. Ruby red complex **1** was obtained as translucent crystals by sublimation at 250 °C and 10^{-6} mbar (1.42 g, 74%).

Method B. An excess of titanium tetrachloride was added dropwise to a stirred solution of H_2L (500 mg, 0.78 mmol) in toluene (20 ml). The deep red mixture was stirred for 16 h. Removal of the volatile components of the reaction mixture under reduced pressure followed by sublimation of the solid residue at 250 °C and 10^{-6} mbar gave complex **1** (560 mg, 94%).

Method C. Boron trichloride (0.3 ml of a 1.0 M solution in hexanes, 0.3 mmol) was added to a solution of $[TiL(NMe_2)_2]$ (250 mg, 0.3 mmol) in pentane which had been cooled to −80 °C. An orange solid was immediately precipitated. The mixture was allowed to warm to room temperature with stirring, after which the solvent and volatile side products were removed under reduced pressure. The remaining solid was recrystallised from the minimum quantity of toluene, giving red complex **1** (180 mg, 79%) (Found C, 68.96; H, 7.12; N, 3.75. $C_{44}H_{54}Cl_2N_2O_2Ti$ requires C, 69.38; H, 7.15; N, 3.68%). ^1H NMR (CD_2Cl_2):† α-*cis*-**1** (aliphatic region only) δ 2.38 (Me), 1.56 (s, Bu^t) and 1.36 (s, Bu^t); β-*cis*-**1** δ 8.44 (s, N=CH), 8.28 (s, N=CH), 7.78 (d, phenolic), 7.65 (d, phenolic), 7.54 (d, phenolic), 7.43 (t, biaryl), 7.33 (m, biaryl and phenolic), 7.23 (d, biaryl), 7.19–7.12 (m, biaryl and phenolic), 6.62 (d, biaryl), 2.23 (s, Me), 2.01 (s, Me), 1.54 (s, Bu^t), 1.41 (s, Bu^t), 1.40 (s, Bu^t) and 1.36 (s, Bu^t). ^{13}C-{^1H} NMR (CD_2Cl_2): β-*cis*-**1** δ 167.66, 166.54 (N=C), 161.65, 161.02, 151.71, 150.36, 144.49, 138.38, 137.08, 136.36, 135.86, 131.81, 131.68, 129.92, 129.77, 129.01, 128.74, 128.62, 128.30, 125.95, 123.73, 122.75, 121.56 (aromatic), 35.30, 34.63 (*C*Me₃), 31.20, 31.07, 29.64 (C*Me*₃), 19.79, 19.76 (Me). IR (Nujol, cm^{-1}): 1608m, 1557, 1544m, 1268, 1250m, 1208, 1180, 1133, 1103, 1026, 972, 948, 916, 876, 848m, 827, 770, 754, 736, 722, 642, 612, 582m, 529 and 483. MS (EI): *m*/*z* 760 [M^+], 725 [M^+ − Cl] and 690 [M^+ − 2Cl].

$[TiLBr_2]$ 2. A solution of $[Na_2(THF)_n][L]^2$ (1.00 g, 1.25 mmol) in diethyl ether (20 ml) was added dropwise to a solution of titanium tetrabromide (0.50 g, 1.31 mmol) in the same solvent (10 ml). Removal of the solvent under reduced pressure and extraction of the solid into toluene gave a red solution which was filtered through Celite and cooled to −40 °C to yield crimson complex **2**. An analytically pure sample was obtained by sublimation at 250 °C and 10^{-6} mbar (1.03 g, 92%) (Found C, 62.30; H, 6.70; N, 3.24. $C_{44}H_{54}Br_2N_2O_2Ti$ requires C, 62.13; H, 6.40; N, 3.29%). ^1H NMR (d^8-toluene): δ 8.39 (s, N=CH), 8.14 (s, N=CH), 8.09 (s, N=CH), 7.80 (d, phenolic), 7.76 (d, phenolic), 7.63 (d, phenolic), 7.42 (d, biaryl), 7.19 (t, biaryl), 7.03–6.90 (m, biaryl and phenolic), 6.71 (d, biaryl), 6.65 (t, biaryl), 6.52 (d, biaryl), 6.27 (d, biaryl), 1.97 (s, Me), 1.85 (s, Me), 1.77 (s, Bu^t), 1.72 (s, Bu^t), 1.72 (s, Me), 1.61 (s, Bu^t), 1.21 (s, Bu^t), 1.18 (s, Bu^t) and 1.07 (s, Bu^t). ^{13}C-{^1H} NMR (d^5-pyridine): δ 169.77, 168.80, 167.63 (N=C), 161.41, 161.07, 151.46, 150.99, 150.42, 144.81, 144.41, 144.07, 137.58, 136.56, 135.77, 135.65, 131.23, 131.10, 130.39, 130.12, 129.90, 129.49, 129.37, 129.13, 128.41, 128.19, 128.11, 127.83, 126.89, 126.01, 124.88, 121.82 (aromatic), 35.48, 34.99, 34.08, 34.01, 33.91 (*C*Me₃), 30.63, 30.59, 30.37, 29.88, 29.69 (C*Me*₃), 19.11, 19.09 (Me). MS (EI): *m*/*z* 769 [M^+ − Br] and 690 [M^+ − 2Br].

$[TiL(NMe_2)_2]$ 3. A solution of $[Ti(NMe_2)_4]$ (200 mg, 0.89 mmol) in pentane (10 ml) was added dropwise to a solution of H_2L (576 mg, 0.89 mmol) in the same solvent (20 ml). The mixture turned red over the course of the addition. It was stirred for 16 h during changing to brown. Removal of the solvent and liberated $NHEt_2$ under reduced pressure gave a green solid which was recrystallised from toluene to yield green complex **3** (489 mg, 70%) (Found C, 73.41; H, 8.40; N, 7.00. $C_{48}H_{66}N_2O_2Ti$ requires C, 74.10; H, 8.54; N, 7.19%). ^1H NMR (C_6D_6): δ 7.77 (s, 2H, C=NH), 7.51 (d, 2H, phenolic), 7.35 (d, 2H, biaryl), 7.04 (t, 2H, biaryl), 6.77 (d, 2H, phenolic), 6.56 (d, 2H, biaryl), 3.36 (s, 12H, NMe), 1.78 (s, 18H, Bu^t), 1.70 (s, 6H, Me) and 1.14 (s, 18H, Bu^t). ^{13}C-{^1H} NMR (C_6D_6): δ 165.00 (N=C), 164.04, 151.76, 138.49, 137.63, 136.47, 131.02, 129.48, 127.54, 126.75, 121.97, 120.2 (aromatic), 48.46 (NMe), 35.69, 33.97 (*C*Me₃), 31.52, 30.39 (C*Me*₃) and 19.90 (Me). IR (Nujol, cm^{-1}): 1614m, 1535, 1305, 1259, 1202, 1169, 1029, 948, 874, 839, 824, 781, 771 and 736. MS (EI): *m*/*z* 735 [M^+ − NMe_2 + 1], 692 [M^+ − $2NMe_2$ + 2] and 645 [M^+ − $Ti(NMe_2)_2$ + 3].

$[TiL^{Bn}(CH_2Ph)]$ 4. A solution of H_2L (500 mg, 0.775 mmol) in diethyl ether (10 ml) was added dropwise to a solution of $[Ti(CH_2Ph)_4]$ (320 mg, 0.775 mmol) in the same solvent (10 ml). The mixture was stirred for 16 h. Orange complex **4** was precipitated and was collected on a frit, washed with cold diethyl ether (3 × 5 ml) and dried *in vacuo*. A second crop was obtained by reducing the volume of the combined liquors and cooling to −30 °C (340 mg, 50%) (Found C, 79.49; H, 7.85; N, 3.15. $C_{58}H_{68}N_2O_2Ti$ requires C, 79.79; H, 7.85; N, 3.21%). ^1H NMR (C_6D_6): δ 8.35 (s, 1H, C=NH), 7.66 (d, 1H, phenolic), 7.50 (d, 1H, phenolic), 7.28 (d, 1H, phenolic), 7.12–6.31 (m, 18H, biaryl, phenolic, benzyl, C*H*CH₂Ph), 3.23 (dd, 1H, CC*H*₂Ph), 3.01 (d, 1H, TiC*H*₂Ph), 2.86 (dd, 1H, CC*H*₂Ph), 2.67 (d, 1H, TiC*H*₂Ph), 2.06 (s, 3H, Me), 1.91 (s, 3H, Me), 1.82 (s, 9H, Bu^t), 1.56 (s, 9H, Bu^t), 1.27 (s, 9H, Bu^t) and 1.26 (s, 9H, Bu^t). ^{13}C-{^1H} NMR (C_6D_6): δ 168.49 (C=N), 163.44, 162.45, 153.90, 147.46, 147.20, 142.01, 141.55, 139.87, 138.63, 136.95, 134.64, 132.71, 132.60, 130.87, 129.73, 129.17, 128.99, 128.83, 128.59, 128.55, 128.12, 128.08, 127.89, 127.68, 127.64, 127.14, 127.09, 125.92, 122.70, 122.53, 122.33, 121.96, 120.71, 120.42, 115.26, 106.07 (aromatic), 80.81 (Ti*C*H₂Ph), 62.56 (NCH), 37.04 (C*C*H₂Ph), 35.96, 35.83, 34.70, 34.26 (*C*Me₃), 31.88, 31.66, 31.44, 30.25 (C*Me*₃), 20.05, 19.60 (Me). IR (Nujol, cm^{-1}): 1613s, 1590, 1559, 1545, 1339, 1294, 1272, 1252m, 1224m, 1205, 1174, 1128, 1086, 1060, 1030, 989, 928, 852, 834, 799, 776, 758, 740, 722, 695, 630, 586, 570, 562, 554, 540, 500 and 482. MS (EI): *m*/*z* 817, 781 [M^+ − CH_2Ph], 725 and 690 [M^+ − $2CH_2Ph$].

$[\{Ti(HL^{Bn})\}_2(\mu\text{-}O)_2]$ 5. A solution of complex **4** (250 mg, 0.286 mmol) in diethyl ether (10 ml) was allowed to stand in a Schlenk tube. Air was admitted through a streaky joint. A change occurred from orange to yellow. Yellow crystals of **5** precipitated on standing at room temperature over several days (170 mg, 72%) (Found C, 76.13; H, 7.58; N, 3.16. $C_{56}H_{61}N_2O_3Ti$ requires C, 76.77; H, 7.70; N, 3.16%). ^1H NMR (C_6D_6): δ 7.79 (s, 2H, N=CH), 7.67 (d, 2H, phenolic), 7.48 (d, 2H, phenolic), 7.41 (d, 2H, phenolic), 7.33 (d, 2H, biaryl), 7.11–7.07 (m, 10H, benzyl), 7.03 (d, 2H, biaryl), 6.85 (d, 2H, phenolic), 6.62 (t, 2H, biaryl), 6.44 (t, 2H, biaryl), 6.31 (d, 2H, biaryl), 5.79 (t, 2H, C*H*CH₂Ph), 5.25 (d, 2H, NH), 3.54 (dd, 2H, C*H*₂Ph), 3.35 (dd, 2H, C*H*₂Ph), 1.77 (s, 6H, Me), 1.72 (s, 18H, Bu^t), 1.65 (s, 18H, Bu^t), 1.38 (s, 6H, Me), 1.35 (s, 18H, Bu^t) and 1.26 (s, 18H, Bu^t). ^{13}C-{^1H} NMR (C_6D_6): δ 169.87 (C=N), 163.10, 161.64, 153.33, 142.21, 140.28, 140.18, 139.13, 138.02, 137.99, 136.08, 134.90,

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† NMR spectra for complexes **1** and **2** are for a mixture of isomers unless otherwise stated (see Results and discussion).

130.53, 129.62, 129.18, 128.79, 128.44, 127.29, 125.97, 124.50, 123.65, 123.34, 121.86, 121.13, 117.35, 115.26, 111.47 (aromatic), 53.28 (N*C*CH_2Ph), 35.93 (*C*Me_3 and *C*H_2Ph), 35.63, 34.58, 34.10 (*C*Me_3), 32.44, 31.97, 31.46, 30.65 (C*Me_3*), 20.08, 19.22 (Me). IR (Nujol, cm^{-1}): 3269, 2722, 2360, 1733, 1612m, 1552, 1539, 1308, 1258m, 1199, 1166, 1072, 973, 925, 872, 847, 826, 801, 783, 756, 734m, 699m, 650, 585, 571, 561, 547, 533 and 464. MS (EI): *m*/*z* 817 [M^+ − {H}L^4 + 3], 782 [M^+ − {H}$L^{Bn}TiO_2$], 725 and 691.

Crystallography

Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Enraf-Nonius CAD4 for complex **2** and Siemens SMART three-circle diffractometer with CCD area detector for **4** and **5**). The structures were solved by direct methods (SHELXS[6]) with additional light atoms found by Fourier methods, and refined using SHELXL 93 (**2**) or SHELXTL (**4** and **5**).[7] In **2** the C(27) and C(28) methyl groups were included as disordered equally between two orientations related by 60° rotation about the C–C bond. In **5** attempts to model an apparent positional disorder in one *tert*-butyl group were not successful. Crystals of **4** and **5** were quite poorly diffracting and the resulting solutions have relatively high *R* values.

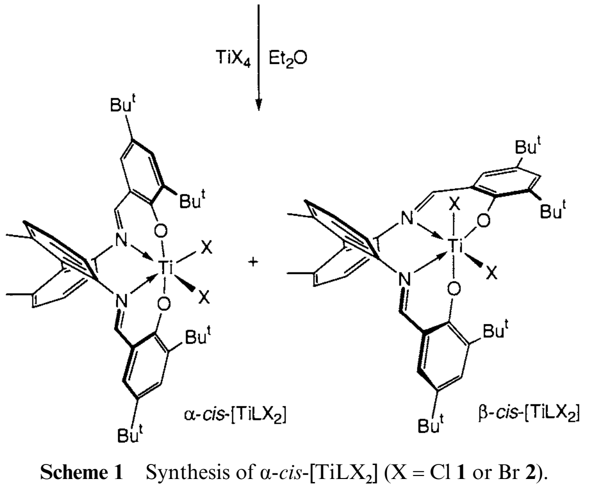
CCDC reference number 186/2137.

See http://www.rsc.org/suppdata/dt/b0/b004865h/ for crystallographic files in .cif format.

Results and discussion

Synthesis of [$TiLX_2$] (X = Cl 1 or Br 2)

Addition of a solution of [$Na_2(THF)_n$][L][2] in diethyl ether to a stoichiometric quantity of $TiCl_4$ in the same solvent resulted in an immediate change to deep red. Removal of the solvent under reduced pressure and sublimation gave the isomeric mixture [$TiLCl_2$] **1** in 74% yield (Scheme 1). The reaction between $TiCl_4$ and H_2L in toluene also gave **1**.



Scheme 1 Synthesis of α-*cis*-[$TiLX_2$] (X = Cl **1** or Br **2**).

The ^1H NMR spectrum of complex **1** is considerably more complicated than that of the zirconium analogue previously described[2] and is consistent with the formation of a mixture of two isomeric forms, *i.e.* the C_2-symmetric α-*cis*-**1** and the C_1-symmetric β-*cis*-**1**. In β-*cis*-**1** all the *tert*-butyl and methyl groups are in different environments, giving rise to a total of six resonances in the aliphatic region. Symmetric α-*cis*-**1** contains only two *tert*-butyl and one methyl environment, giving a total of nine resonances for the mixture, as observed. The ratio of α-*cis*-**1** : β-*cis*-**1** initially formed is *ca.* 1 : 2. Holding the temperature of an NMR sample at 50 °C for 3 h did not lead to a significant change in this ratio. The two isomers appear to have very similar solubilities in diethyl ether and toluene since this ratio is essentially unchanged by recrystallisation from those solvents. Sublimation of the mixture also does not afford any change in the relative proportions.

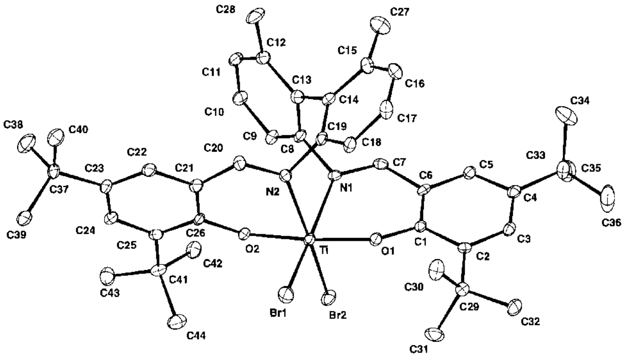


Fig. 1 Thermal ellipsoid plot of the molecular structure of complex **2**; hydrogen atoms omitted.

[$TiLBr_2$] **2** was synthesized by the reaction between [$Na_2(THF)_n$][L] and $TiBr_4$ in diethyl ether. A mixture of isomers α-*cis*-**2**/β-*cis*-**2** was produced as above. A single crystal of α-*cis*-**2** was obtained by heating a sample of **2** in an evacuated, sealed tube at 250 °C. An X-ray crystallographic investigation of this crystal resulted in the molecular structure shown in Fig. 1. A single crystal containing the isomer β-*cis*-**2** could not be found. Crystallographic data are given in Table 1 and selected bond lengths and angles in Table 2. Although α-*cis*-**2** does not possess a crystallographic C_2 axis, the main structural features are the same as those of [$ZrLCl_2$], with the metal in a pseudo-octahedral co-ordination environment, mutually *cis* imine nitrogen atoms and bromide ligands, and *trans* phenolate oxygens. A comparison of the bond lengths of α-*cis*-**2** and [$ZrLCl_2$] (Table 2) reveals that the M–N and M–O bonds are significantly shorter in the former, concomitant with the smaller size of titanium compared to zirconium. The Ti–N and Ti–O distances in α-*cis*-**2** are very similar to those in the titanium(IV) Schiff base complex [Ti(acen)Cl_2] [acen = *N*,*N*′-ethylenebis(acetylacetoneiminate)].[8] The Ti–N distance is marginally longer in α-*cis*-**2** [2.186(0) Å, average] compared to that in [Ti(acen)Cl_2] [2.129(2) Å, average] which is probably a result of the imine nitrogen atoms being *trans* to chloride ligands in the former but *trans* to phenol oxygens in the latter. The angle Br(1)–Ti–Br(2) at 103.60(6)° is very similar to that observed for Cl–Zr–Cl′ in α-*cis*-[$ZrLCl_2$] [103.56(3)°], despite the larger halogen atom and smaller metal in **2**. Other angles about the metal in these structures are also quite similar, but the largest differences (particularly the O–M–O′ and smaller O–M–N angles) indicate that ring strain in **2** is tending to distort the structure in the direction of a more conventional planar arrangement.

This latter phenomenon is also manifest in the observation of β-*cis* isomer in samples of complex **2**. In the analogous zirconium chemistry no β-*cis* isomers of halides or other derivatives have been observed. That this form has greater stability in the titanium compounds is thus most probably due to the smaller ionic radius of the first row metal and concomitant increase in ring strain energy. Nevertheless, the β-*cis* isomer appears on the basis of space-filling models to be more sterically encumbered, and in accord with this we have shown that a complex containing bulkier amido co-ligands forms the α-*cis* isomer only (see below).

Synthesis of α-*cis*-[$TiL(NMe_2)_2$] 3

The reaction between the isomeric mixture **1** and $LiNMe_2$ in toluene, or between H_2L and [$Ti(NMe_2)_4$] in light petroleum (bp 40–60 °C), gave the dark green bis(dimethylamido) derivative [$TiL(NMe_2)_2$] **3** in *ca.* 70% yield. The ^1H NMR spectrum

Table 1 Experimental data for the X-ray diffraction studies of complexes **2**, **4**, and **5**·$\frac{1}{2}C_5H_{12}$

	2	**4**	**5**·$\frac{1}{2}C_5H_{12}$
Molecular formula	$C_{44}H_{54}Br_2N_2O_2Ti$	$C_{58}H_{68}N_2O_2Ti$	$C_{53.5}H_{67}N_2O_3Ti$
Formula weight	850.6	873.04	833.99
T/K	173(2)	293(2)	180(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	10.190(7)	19.7558(10)	14.270(3)
b/Å	13.442(3)	10.2159(5)	16.917(3)
c/Å	16.376(6)	26.3957(13)	22.645(4)
α/°	80.13(2)	—	89.2150(10)
β/°	82.40(4)	99.6850(10)	86.8140(10)
γ/°	71.27(4)	—	79.7910(10)
V/Å^3	2086(2)	5251.3(5)	5371.9(16)
Z	2	4	4
μ/mm^{-1}	2.16	0.204	0.198
Total reflections	5780	20157	21842
Independent reflections	4269	6819	13915
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.049, 0.103	0.1005, 0.2521	0.1109, 0.2739

Table 2 Selected bond distances (Å) and angles (°) for $[TiLBr_2]$ **2** compared with those of $[ZrLCl_2]$[2]

	$[TiLBr_2]$ **2**	$[ZrLCl_2]$[a]
Ti–O(1)	1.870(3)	2.009(1)
Ti–O(2)	1.867(3)	
Ti–N(1)	2.188(4)	2.316(2)
Ti–N(2)	2.184(4)	
Ti–Br(1)	2.448(2)	
Ti–Br(2)	2.457(2)	
Br(1)–Ti–Br(2)	103.60(6)	103.56(3)[b]
O(2)–Ti–O(1)	174.6(2)	171.95(8)
O(2)–Ti–N(2)	80.9(2)	76.42(6)
O(1)–Ti–N(2)	97.1(2)	97.11(6)
O(2)–Ti–N(1)	93.4(2)	
O(1)–Ti–N(1)	81.2(2)	
N(2)–Ti–N(1)	76.7(2)	75.66(8)
O(2)–Ti–Br(1)	92.96(11)	93.36(5)[b]
O(1)–Ti–Br(1)	92.08(11)	
O(2)–Ti–Br(2)	90.01(11)	91.62(5)[b]
O(1)–Ti–Br(2)	90.79(11)	
N(2)–Ti–Br(1)	89.01(12)	91.76(5)[b]
N(1)–Ti–Br(1)	163.22(11)	
N(2)–Ti–Br(2)	164.90(11)	162.07(11)[b]
N(1)–Ti–Br(2)	91.90(12)	

[a] This structure has a crystallographic C_2 axis so there are fewer unique parameters. [b] Angle to Cl atom(s).

contains two *tert*-butyl resonances (δ 1.78 and 1.14 ppm), one methyl resonance (δ 1.70) and one resonance for the amido methyl protons (δ 3.36). Thus only the α-*cis* isomer is present in solution. The absence of the unsymmetric β-*cis* isomer of **3** is more probably due to the steric demand of the two dimethylamido groups (see above) than an electronic preference for placing the amide ligands *trans* to imine.

If an excess of BCl_3 is added to a solution of complex **3** in light petroleum at −78 °C an orange precipitate of **1** forms immediately. Despite the presence of only one isomer of **3**, this precipitate is found to be a mixture of α-*cis*-**1** and β-*cis*-**1**.

Attempts to alkylate $[TiLCl_2]$ 1

Various outcomes have been reported for the reaction of titanium Schiff base complexes with alkylating agents, including reduction at the metal centre or addition to the ligand imine group, with the choice of solvent being critical in dictating the reactivity observed.[4] We made numerous attempts to synthesize alkyl derivatives of the [TiL] fragment, involving reactions between **1** and reagents such as methyllithium, phenyllithium, cyclopentadienyllithium, $LiCH(SiMe_3)_2$, and KCH_2Ph, and in solvents such as pentane, diethyl ether and benzene. Reactions were also attempted in the presence of stronger donor solvents such as THF and pyridine. In no case could a tractable product be isolated from the reaction mixture. ^{1}H NMR spectra of the resulting mixtures contained significantly broadened resonances compared to those of the starting materials. This suggests that **1** may be susceptible to either partial or complete reduction to titanium(III) species in the course of the reactions, although no pure complex of Ti^{III} has been identified or isolated.

Attempts to synthesize titanium(III) complexes containing L

It has been found that alkylation reactions of titanium Schiff base complexes proceed in a more straightforward manner when the metal centre is in a formal oxidation state of +3 rather than +4,[9] and this has also been noted for vanadium.[10] The synthesis of complexes of Ti^{III} containing L was attempted by reduction of **1** and by reaction of $[TiCl_3(THF)_3]$ with $[Na_2(THF)_n][L]$. The former route led to mixtures of paramagnetic products and the latter to the isolation of low yields of **1** presumably *via* disproportionation. A similar reaction has been reported by Bowden and Ferguson who obtained the complex [Ti(salphen)Cl_2] from the reaction between H_2(salphen) [*N*,*N*′-bis(salicylidene)-*o*-phenylenediamine] and $[TiCl_3(THF)_3]$.[11]

Reaction of H_2L with $[Ti(CH_2Ph)_4]$

The failure to alkylate complex **1** with conventional nucleophilic alkylating agents led us to explore the reaction between the homoleptic titanium alkyl $[Ti(CH_2Ph)_4]$ and the protonated form of the ligand H_2L. Dropwise addition of a solution of H_2L in diethyl ether to a stoichiometric quantity of $[Ti(CH_2Ph)_4]$ in the same solvent results in a change to dark orange over a period of *ca.* 12 h and the precipitation of a bright orange microcrystalline solid which was collected and dried. The characterising data for this material indicate that co-ordination of L to titanium has been accompanied by the highly diastereoselective migration of a benzyl group from the metal centre to one imine carbon of the ligand, resulting in a new trianionic ligand (hereafter denoted L^{Bn}) bound to a Ti–CH_2Ph fragment in the complex [TiL^{Bn}(CH_2Ph)] **4** (Scheme 2). In another system, Floriani and co-workers have reported the alkylation of the imine groups of a dibenzotetramethyltetraazaannulene complex of Zr^{IV}.[12]

When the synthesis of complex **4** was performed in C_6D_6 the ^{1}H NMR spectrum recorded after 5 min showed in the region δ 2.5–3.5 a pair of AB doublets which may be attributed to the intermediate α-*cis*-$[TiL(CH_2Ph)_2]$. Signals for the Schiff-base ligand in a C_2-symmetric α-*cis* arrangement were assigned

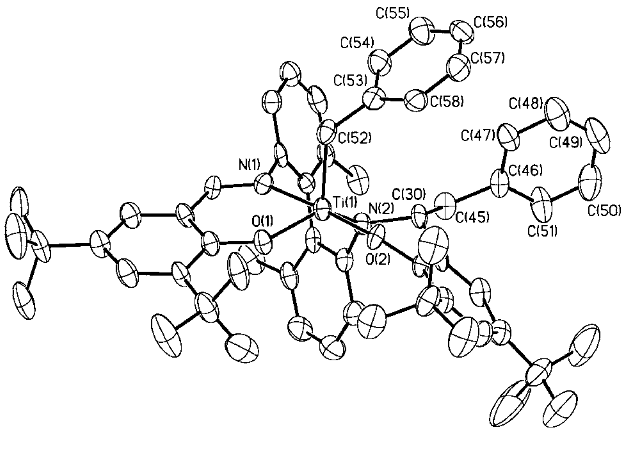
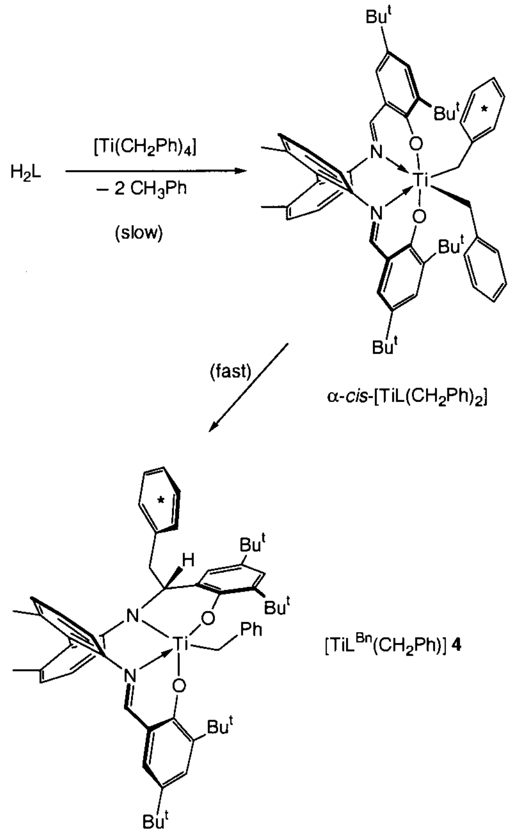


Fig. 2 Thermal ellipsoid plot of the molecular structure of complex **4**; hydrogen atoms omitted.



Scheme 2 Synthesis of complex **4** *via* the observed intermediate $[TiL(CH_2Ph)_2]$.

readily. Conversion of this species into **4** is rapid however, and attempts to isolate the dialkyl were unsuccessful.

The migration of a benzyl group (marked ★ in Scheme 2) from metal to ligand results in the generation of a new stereogenic centre. However, there is no evidence from ^{1}H NMR spectroscopy of more than one diastereomer being formed. If the reaction is carried out at room temperature in d_8-toluene the ^{1}H spectrum recorded after 24 h shows the main product to be present in *ca.* 80% purity, with the remaining peaks in the spectrum being unassigned but not consistent with the second diastereomer of the product. The same experiment conducted at 0 °C led to exclusive formation of diastereomerically pure **4**. This extremely high diastereoselectivity arises from the lack of a stereochemically accessible pathway for migration of a benzyl group to the other enantiotopic face of the imine group in either an intra- or inter-molecular sense.

Table 3 Selected bond distances (Å) and angles (°) for complex **4**

Ti(1)–O(2)	1.880(5)	Ti(1)–C(52)	2.112(7)
Ti(1)–N(2)	1.881(6)	Ti(1)–N(1)	2.246(6)
Ti(1)–O(1)	1.893(5)	N(2)–C(30)	1.503(9)
O(2)–Ti(1)–N(2)	89.8(2)	O(1)–Ti(1)–C(52)	109.2(3)
O(2)–Ti(1)–O(1)	102.1(2)	O(2)–Ti(1)–N(1)	171.4(2)
N(2)–Ti(1)–O(1)	131.3(2)	N(2)–Ti(1)–N(1)	82.4(2)
O(2)–Ti(1)–C(52)	97.2(3)	O(1)–Ti(1)–N(1)	80.6(2)
N(2)–Ti(1)–C(52)	115.9(3)	C(52)–Ti(1)–N(1)	89.6(3)

The aliphatic region of the ^{1}H NMR spectrum of complex **4**, which contains four peaks assigned to *tert*-butyl groups and two peaks assigned to methyl groups, is consistent with C_1 symmetry. The single remaining N=CH proton resonates at δ 8.35. The methylene protons of the benzyl group bound directly to the metal centre are mutually coupled in the unsymmetrical environment and give rise to a pair of AB doublets at *ca.* δ 3.01 and 2.67. Similarly, the diastereotopic CH_2 protons of the benzyl group bound to the ligand are coupled to one another and also to the α-amido proton ($J^3 = 11$ and 2 Hz respectively). This gives rise to a pair of doublets of doublets, centred at δ 3.23 and 2.86. The resonance for the α-amido proton itself has been located using ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectra, and at δ *ca.* 6.9 is masked by aromatic peaks.

Single crystals of complex **4** were grown from a concentrated solution in dichloromethane layered with acetonitrile, and subjected to an X-ray crystallographic investigation. The resulting structure is shown in Fig. 2. Selected bond lengths and angles are shown in Table 3. The co-ordination environment about titanium is best described as distorted trigonal bipyramidal. The equatorial plane of the bipyramid is composed of the amide nitrogen, N(2), one phenol oxygen, O(1), and the benzyl carbon C(52). The equatorial positions are completed with the imine nitrogen N(1) and the second phenol oxygen O(2). The ligating nitrogen atoms remain mutually *cis*, as dictated by the biphenyl backbone, but one phenol oxygen is *trans* to the imine nitrogen atom, rather than being *trans* to the other oxygen atom as in most complexes of L. The existence of two distinct types of Ti–N bonds in **4** can readily be appreciated from the bond lengths, which are 1.881(6) Å for the Ti(1)–N(2) amide bond and 2.246(6) for the Ti(1)–N(1) imine bond. The former value is typical of Ti–N(amide) bond lengths in a variety of other titanium(IV) amido complexes,[13,14] and the latter is slightly longer than is typical in titanium(IV) Schiff base complexes[4,8] (including **2**) presumably as a consquence of the constraints within the chelate system. The bond angles about both N(1) and N(2) suggest sp^2 hybridisation, although with slight distortions from trigonal planar geometry. The Ti–C(52) distance of 2.112(7) Å is comparable to that found in other titanium benzyl complexes,[14,15] and the Ti–C(52)–C(53) angle of 122.3(5)° combined with the Ti–C(53) distance of *ca.* 3.17 Å indicates η^1-benzyl co-ordination.

As was the case for $[ZrL(OPh)_2]$,[2] it appears that there are edge-to-face aromatic interactions in the solid state structure of complex **4**. The phenyl ring of the "migrated" benzyl group is oriented such that an *ortho* C–H bond at C(47) is pointing towards the centre of the metal bound benzyl ring. The C–H–ring centroid angle of *ca.* 165° (based on the calculated position of the H atom) and centroid–centroid distance *ca.* 5.12 Å are close to the calculated optimum for such interactions.[16] There also appears to be a weaker interaction between the metal bound benzyl group and one of the biphenyl rings. These interactions are illustrated in Fig. 3.

Reaction of complex 4 with water: synthesis of $[\{Ti(HL^{Bn})\}_2(\mu\text{-}O)_2]$ 5

When a Schlenk tube containing a solution of complex **4** in diethyl ether was exposed to air the solution changed from

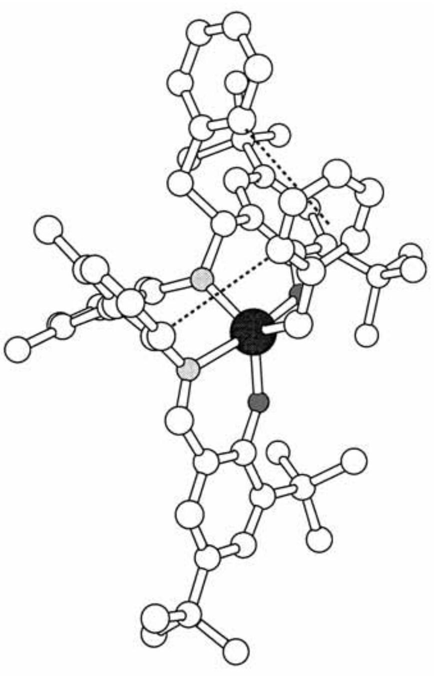
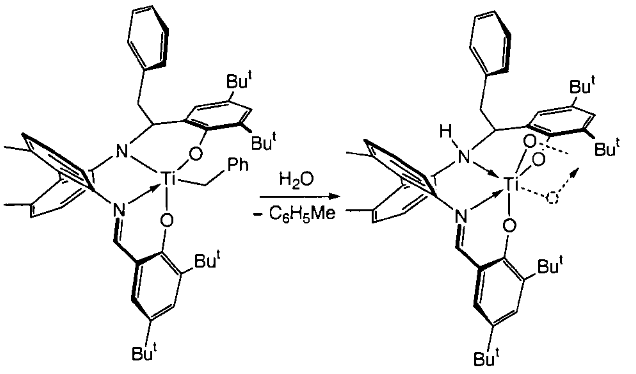


Fig. 3 Molecular structure of complex **4** showing the non-covalent contacts between arene groups.

orange to yellow. On further standing, yellow crystals of the oxo-bridged dimer [{Ti(HL^{Bn})}$_2$(μ-O)$_2$] **5** precipitated (Scheme 3). This reaction is entirely reproducible, and also occurs when **4** is dissolved in undried degassed solvents.



Scheme 3 Hydrolysis of complex **4** to the oxo-bridged dimer **5**.

The ^{1}H NMR spectrum of complex **5** contains four resonances assigned to *tert*-butyl groups and two to methyl groups indicating that the two halves of the dimer are equivalent on this chemical shift timescale. The benzyl CH$_2$ region of the spectrum (δ 3–4) contains two multiplets which are very similar in appearance to those in a spectrum of **4** and are assigned to the diastereotopic protons of the ligand bound benzyl group. However, a pair of simple AB doublets for titanium bound benzyl methylene protons were no longer observed. The resonance for the proton of the reduced imine group occurs as a second order 1 : 1 : 1 triplet at δ 5.79, and that is in turn coupled to a doublet at δ 5.25. This resonance, which has no equivalent in the spectrum of **4**, is assigned to a proton arising from the conversion of the amido functionality in L^{Bn} into a secondary amine group by protonation by atmospheric moisture. This is supported by the appearance of a ν(N–H) peak at 3269 cm^{-1} in the IR spectrum. There is no band at comparable wavenumber in the IR spectrum of **4**.

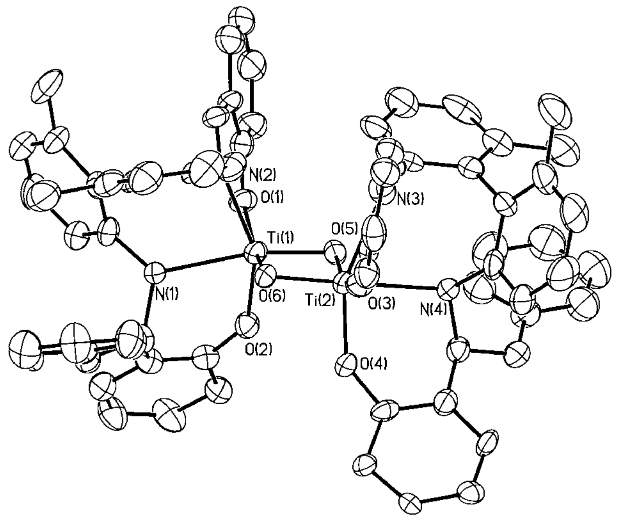


Fig. 4 Thermal ellipsoid plot of the molecular structure of complex **5**; hydrogen atoms and *tert*-butyl groups omitted for clarity.

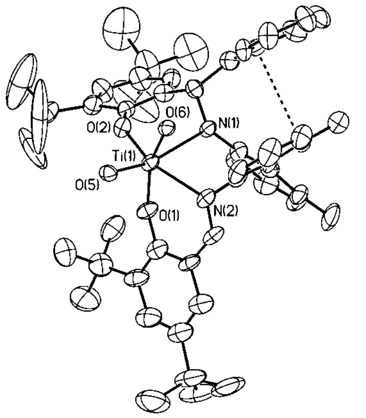


Fig. 5 Molecular structure of the Ti(HL^{Bn})O$_2$ unit surrounding Ti(1) in complex **5**. Atoms O(5) and O(6) are bridging to Ti(2) (see Fig. 4).

Single crystals of complex **5** were been obtained by allowing a saturated solution in diethyl ether to stand at room temperature for a period of days. The molecular structure as determined by X-ray crystallography is shown in Fig. 4, and the ligature surrounding Ti(1) is shown in Fig. 5. That surrounding Ti(2) is very similar, and it is noteworthy that the absolute configurations of the ligands in both halves of the dimer are the same. The H atoms at amine nitrogen atoms N(1) and N(4) were not located in difference maps, but evidence for protonation (sp^3 hybridisation) comes from the fact that the sums of angles (*ca.* 348 and 345°) are rather less than the *ca.* 360° measured for the planar imino atoms N(2) and N(3). The amine Ti(1)–N(1) and Ti(2)–N(4) distances at 2.393(7) and 2.455(7) Å (Table 4) are comparable with others measured,[17] and rather longer than the Ti–N(amide) distance of 1.882(6) Å in **4**. The bridging oxo units are slightly unsymmetrical with Ti–O distances of between 1.778(5) and 1.925(6) Å. In a titanium Schiff base dimer with a linear bridging oxo ligand, reported by Mazzanti *et al.*,[8] the Ti–O distance is 1.813(1) Å. Other bond lengths in **5** are similar to those in **4**. It can be seen from Fig. 5 that the "migrated" benzyl group is oriented face-to-face with one of the backbone arenes (*cf.* Fig. 3).

Conclusion

The stereochemistry adopted in biaryl-bridged Schiff-base (L) complexes of the Group 4 metals depends on two factors. First, for the smaller ion Ti there is a tendency to form the unsymmetric β-*cis* isomer in order to relieve ring strain. Secondly, bulky auxiliary ligands will tend to stabilise the α-*cis*

Table 4 Selected bond distances (Å) and angles (°) for complex **5**

Ti(1)–O(5)	1.795(6)	Ti(2)–O(6)	1.778(5)
Ti(1)–O(2)	1.869(6)	Ti(2)–O(4)	1.885(6)
Ti(1)–O(6)	1.925(6)	Ti(2)–O(3)	1.922(6)
Ti(1)–O(1)	1.926(6)	Ti(2)–O(5)	1.923(6)
Ti(1)–N(2)	2.302(7)	Ti(2)–N(3)	2.265(7)
Ti(1)–N(1)	2.393(7)	Ti(2)–N(4)	2.455(7)
Ti(1) · · · Ti(2)	2.779(2)		
O(5)–Ti(1)–O(2)	96.5(3)	O(5)–Ti(1)–Ti(2)	43.42(19)
O(5)–Ti(1)–O(6)	82.6(2)	O(2)–Ti(1)–Ti(2)	100.18(19)
O(2)–Ti(1)–O(6)	103.3(3)	O(6)–Ti(1)–Ti(2)	39.40(16)
O(5)–Ti(1)–O(1)	99.1(3)	O(1)–Ti(1)–Ti(2)	139.85(19)
O(2)–Ti(1)–O(1)	97.8(3)	N(2)–Ti(1)–Ti(2)	98.88(18)
O(6)–Ti(1)–O(1)	158.5(3)	N(1)–Ti(1)–Ti(2)	116.97(18)
O(5)–Ti(1)–N(2)	109.3(3)	O(6)–Ti(2)–Ti(1)	43.41(19)
O(2)–Ti(1)–N(2)	154.3(3)	O(4)–Ti(2)–Ti(1)	97.99(18)
O(6)–Ti(1)–N(2)	81.1(3)	O(3)–Ti(2)–Ti(1)	141.30(19)
O(1)–Ti(1)–N(2)	78.2(3)	O(5)–Ti(2)–Ti(1)	39.90(17)
O(5)–Ti(1)–N(1)	160.0(3)	N(3)–Ti(2)–Ti(1)	98.50(19)
O(2)–Ti(1)–N(1)	82.1(2)	N(4)–Ti(2)–Ti(1)	119.92(19)
O(6)–Ti(1)–N(1)	78.3(2)	Ti(1)–O(5)–Ti(2)	96.7(3)
O(1)–Ti(1)–N(1)	100.8(3)	Ti(2)–O(6)–Ti(1)	97.2(3)
N(2)–Ti(1)–N(1)	73.9(2)		

isomer. This matter is of relevance to the use of closely related complexes in enantioselective trimethylsilylcyanation of aldehydes.[18]

The alkyl complex [TiL(CH_2Ph)$_2$] is, like its zirconium homologue, unstable. In this case however the decomposition takes the form of a clean and highly diastereoselective 1,2-migratory insertion reaction at one imine group in the complex. This stereoselectivity arises from the well expressed asymmetric environment engendered by the biaryl group and demonstrates clearly a structural basis for the success of such complexes in enantioselective catalysis.[18,19] We are currently exploring the use of complexes such as **4** in organic transformations such as ketone alkylation.

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