Cyclopentadienyl titanium chlorides containing *ortho*-(1-naphthyl)phenoxide ligation

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A series of mono-cyclopentadiene derivatives of titanium containing *ortho*-(1-naphthyl)phenoxide ligands have been studied; the Ti–Ti distance in the d^1 - d^1 species [Cp(Ar-O)Ti(μ -Cl)₂Ti(OAr)Cp] is exactly intermediate between that found in paramagnetic [Cp₂Ti(μ -Cl)₂TiCp₂] and diamagnetic [(ArO)₂Ti(μ -Cl)₂Ti(μ -Cl)₂

Ortho-phenyl phenoxide ligands, *e.g.* **1** (Scheme 1) and **2**, are an important subset of aryloxide ligation that have been used to support inorganic/organometallic chemistry at p-block,¹ d-block² and f-element³ metal centers. Following our successful development of cyclometalation resistant, *e.g.* **3** and **4**, and immune, **5** (Scheme 1) aryloxide ligation⁴ we have begun to study the chemistry of potentially chiral o-(1-naphthyl)phen-



Scheme 1

oxide ligands. Straightforward synthetic strategies lead to the non-symmetric **6** and symmetric **7** and **8** (Scheme 1, Np = 1-naphthyl).[†] Both **7** and **8** are produced as a 50/50 mixture of non-chiral *meso* and DL forms. In the case of **7** inter-conversion of the two forms occurs on the NMR timescale with the barrier for naphthyl rotation estimated as 18.0(5) kcal mol⁻¹ at 67 °C. Presumably a similar barrier will be present for other *o*-(1-naphthyl)phenols lacking *meta* substituents. In the case of *meta*-phenyl blocked **8** it is possible to isolate the pure, crystalline *meso* form from CH₂Cl₂-heptane and show that inter-conversion in this case requires days at 100 °C.⁵ In contrast an adaptation of the chemistry of the late Sir Derek Barton⁶ leads to **9** (Scheme 1) which is produced as a single isomer whose subsequent chemistry (below) shows it to be the chiral form.

Reaction of phenols 1, 4–6 and 9 in the presence of pyridine (py) or the lithium salt of 5 with [CpTiCl₃] yields the compounds 10–12 as orange solids in high yield (Scheme 2). The solid state structure of 12b (Fig. 1)⁺ confirms the chiral nature of the single isomer of phenol 9 generated by the particular method of synthesis. The solution NMR spectroscopic properties of 10–12 are as expected with single C₅H₅ resonances and a single set of aryloxide signals in each cause.[†] In the ¹H NMR spectrum of 12b the C₅H₅ protons resonate at significantly higher field, δ 5.32 compared to the δ 5.6–5.8 region found for the other derivatives. This indicates much greater diamagnetic shielding of adjacent ligand protons and is caused by the presence of the two *ortho*-(1-naphthyl) rings, which are locked in place by the *meta-tert*-butyl groups.

Treatment of **10b** with sodium amalgam (1 Na per Ti) leads to a red solution of the dimeric species **13** (Scheme 2). The solid state structure of **13** (Fig. 2)[‡] shows a dinuclear compound with a Ti(μ -Cl)₂Ti core and terminal aryloxide and Cp groups. The



Table 1 Structural parameters for $[(X)(Y)TiCl_2]$ and $[(X)(Y)Ti(\mu-Cl)_2Ti(X)(Y)]$; X, Y = Cp or ArO (Np = 1-naphthyl)

Compound	X-Ti-Y/°	Cl-Ti-Cl/°	Ti–Cl/Å	Ti–Ti/Å	Ref.
Cp ₂ TiCl ₂	131	94	2.36 (av.)	_	7
CpTi(OC ₆ HNp ₂ -2,6-Bu ^t ₂ -3,5) ₂ Cl ₂ 12b	118	102	2.23 (av.)	—	This work
$Ti(OC_6H_3Ph_2-2,6)_2Cl_2$	109	113	2.206(1)	_	8
$[Cp_2Ti(\mu-Cl)]_2$	133	79	2.55 (av.)	3.95 (av.)	9
$[CpTi(OC_6H_2Np-2-But_2-4,6)(\mu-Cl)]_2$ 13	125	115	2.40 (av.)	3.336(1)	This work
$[Ti(OC_6H_3Ph_2-2,6)_2(\mu-Cl)]_2$	144	102	2.37 (av.)	2.9827(7)	10



Fig. 1 Molecular structure of 12b showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti-O(10) 1.774(3), Ti-Cl(1) 2.230(2), Ti-Cl(2) 2.244(2); Cl-Ti-Cl 102.36(7), Cp-Ti-O(10) 118.6(2), Ti-O(10)-C(11) 164.1(3).



Fig. 2 Molecular structure of 13 showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti-Ti 3.336(1), Ti-O(10) 1.817(2), Ti-Cl(1) 2.400(1), 2.406(1); Cl(1)-Ti-Cl(1) 92.07(4), Cp-Ti-O(10) 125.1(3), Ti-O(10)-C(11) 166.7(2).

Cp ligands are arranged in a transoid fashion, with a crystallographic inversion center being present. The molecular structure of **13** is such that each dimeric unit contains two naphthylphenoxides of opposite chirality.

Table 1 collects some structural parameters for selected derivatives of Ti(IV/III), focusing on the effects of replacing Cp ligands by OAr groups. Some trends can be discerned. The Ti-Cl distance decreases significantly in both series of compounds as Cp is replaced by OAr, reflecting an increase in electrophilicity of the metal center. In the tetrahedral Ti(IV) series the Cl-Ti-Cl angle opens up as the corresponding X-Ti-Y angle closes down upon replacement of Cp by OAr.7,8 The most interesting parameter is the Ti-Ti distances in the d1-d1 dimers.^{9,10} The 3.95(av.) distance in the Cp₂Ti compounds is consistent with the complete lack of any metal-metal bonding. In contrast the short distance in the diamagnetic bis(aryloxide) is consistent with the presence of a Ti-Ti single bond.10 In the case of the 'hybrid' paramagnetic species 13, the Ti-Ti distance is exactly intermediate between the previous two molecules. In this case there is clearly no metal-metal bond present and the observed Ti-Ti distance possibly is purely a consequence of the Ti–Cl distances within the $Ti(\mu$ -Cl)₂Ti unit.

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Notes and references

† Selected spectroscopic data: aromatic signals unless indicated: 1H NMR (C₆D₆, unless otherwise stated, 30 °C): **6**: (CDCl₃) δ 7.00-7.90; 4.82 (s, OH); 1.44 (s), 1.32 [s, C(CH₃)₃]. 7: (CDCl₃) δ 6.80–8.20; 4.78 (s), 4.74 (s, OH). 8: (CDCl₃) δ7.00-8.10; 4.95 (s), 4.93 (s, OH). 9: δ7.9-7.23 (m); 4.15 (s, OH); 1.18 [s, C(CH₃)₃]. 10a: δ 7.22–8.20; 5.60 (s, C₅H₅); 1.67 (s), 1.25 [s, C(CH₃)₃]. **10b**: δ7.20–7.60; 5.70 (s, C₅H₅); 1.63 (s), 1.27 [s, C(CH₃)₃]. 11: δ7.19–7.36; 6.79 (s, para-H); 5.78 (s, C₅H₅); 2.03 (s, meta-CH₃). 12a: δ7.72 (s, para-H); 7.30–7.16 (m); 5.91 (s, C₅H₅); 1.23 [s, C(CH₃)₃]. 12b: δ 7.87 (s, para-H); 7.71–7.13 (m); 5.32 (s, C₅H₅); 1.10 [s, C(CH₃)₃]. ¹³C NMR (C_6D_6 , unless otherwise stated, 30 °C): 6: (CDCl₃) δ 149.3 (O-C); 123.8–141.8; 35.1, 34.4 [$C(CH_3)_3$]; 31.7, 29.7 [$C(CH_3)_3$]. 7: (CDCl₃) δ 150.7, 150.6 (CO); 135.1, 135.0, 133.8, 131.95, 131.88, 127.0, 126.93; 131.3, 129.3, 128.4, 128.3, 128.0, 127.8, 126.3, 126.2, 126.0, 125.9, 125.6, 120.3, 120.2. 8: (CDCl₃) δ 151.43, 151.38 (CO); 124.0–141.0. 9: δ 151.7 (O-C); 148.5, 136.2, 133.5, 129.5, 128.1, 128.0, 126.6, 126.1, 125.9, 125.3, 122.8, 118.0, 109.5; 37.2 [C(CH₃)₃]; 32.4 [C(CH₃)₃]. 10a: δ 165.0 (Ti-O-*C*); 120.6 (*C*₅H₅); 36.0, 34.7 [*C*(CH₃)₃]; 31.5, 30.7 [C(*C*H₃)₃]. **10b**: δ 164.6 (Ti-O-C); 121.1 (C₅H₅); 35.9, 34.7 [C(CH₃)₃]; 31.5, 30.6 [C(CH₃)₃]. 11: δ 164.3 (Ti-O-C); 120.2 (C₅H₅); 20.7 (meta-CH₃). 12a: δ 165.8 (O-C); 147.9, 138.5, 132.9, 131.1, 128.5, 127.8, 121.4; 119.8 (C5H5); 37.5 $[C(CH_3)_3]; 33.0 [C(CH_3)_3].$ **12b**: δ 166.2 (O–C); 149.1, 136.6, 135.5, 134.2, 130.4, 128.8, 128.7, 128.3, 127.3, 126.3, 126.1, 125.3, 122.4; 119.6 (C₅H₅); 37.9 [C(CH₃)₃]; 32.8 [C(CH₃)₃].

[‡] *Crystal data*: for **12b** at 296 K: TiCl₂OC₃₉H₃₈, *M* = 641.54, space group *P*1 (no. 2), *a* = 10.960(1), *b* = 11.644(3), *c* = 15.603(1) Å, *α* = 71.003(7), *β* = 104.23(3), *γ* = 63.402(5)°, *V* = 1673.5(3) Å³, *D_c* = 1.273 g cm⁻³, *Z* = 2. Of the 6851 unique reflections collected (7.69 ≤ 2θ ≤ 62.74°) with Mo-Kα (λ = 0.71073 Å), the 6851 with $F_0^2 > 2\sigma(F_0^2)$ were used in the final least-squares refinement to yield $R(F_0) = 0.076$ and $R_w(F_0^2) = 0.190$. For **13** at 296 K: Ti₂Cl₂O₂C₅₈H₆₄, *M* = 959.86, space group *P*2₁/*n* (no. 14), *a* = 12.5923(5), *b* = 12.7390(6), *c* = 17.4609(8) Å, *β* = 109.814(2)°, *V* = 2635.1(4) Å³, *D_c* = 1.210 g cm⁻³, *Z* = 2. Of the 6836 unique reflections collected (5.90 ≤ 2θ ≤ 61.46°) with Mo-Kα (λ = 0.71073 Å), the 6836 with $F_0^2 > 2\sigma(F_0^2)$ were used in the final least-squares refinement to yield *R*(*F*₀) = 0.169.

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