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

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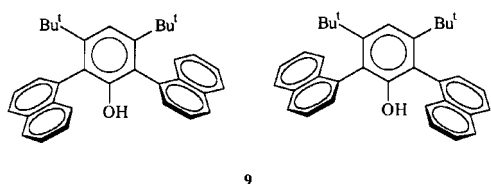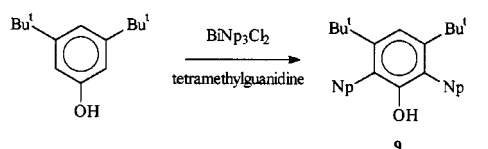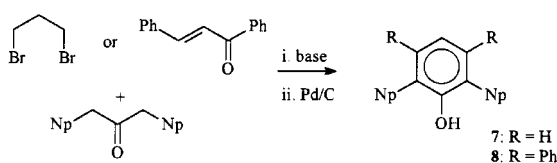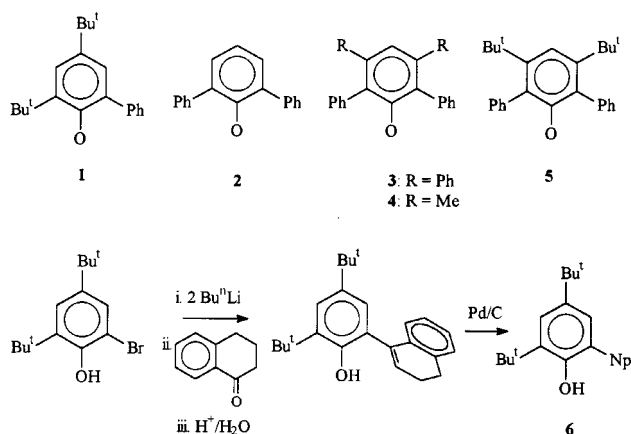*E-mail. rothwell@chem.purdue.edu*

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)$_2$Ti(OAr)Cp] is exactly intermediate between that found in paramagnetic [Cp$_2$Ti(μ-Cl)$_2$TiCp$_2$] and diamagnetic [(ArO)$_2$Ti(μ-Cl)$_2$Ti(OAr)$_2$].

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-block[2] and f-element[3] metal centers. Following our successful development of cyclometalation resistant, *e.g.* **3** and **4**, and immune, **5** (Scheme 1) aryloxide ligation[4] we have begun to study the chemistry of potentially chiral *o*-(1-naphthyl)phen-
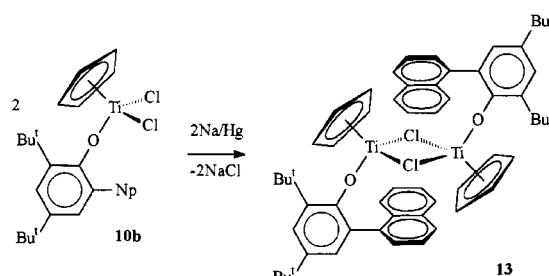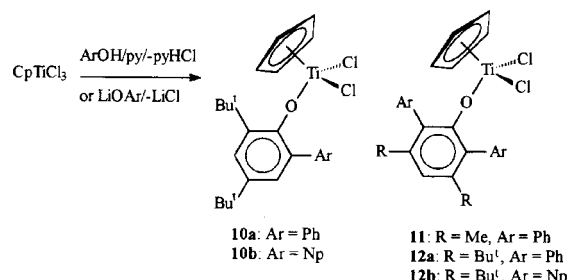
oxide ligands. Straightforward synthetic strategies lead to the non-symmetric **6** and symmetric **7** and **8** (Scheme 1, Np = 1-naphthyl).† Both **7** and **8** are produced as a 50/50 mixture of non-chiral *meso* and DL forms. In the case of **7** inter-conversion of the two forms occurs on the 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 CH$_2$Cl$_2$–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 Barton[6] 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 [CpTiCl$_3$] 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 C$_5$H$_5$ resonances and a single set of aryloxide signals in each cause.† In the ^{1}H NMR spectrum of **12b** the C$_5$H$_5$ 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)$_2$Ti core and terminal aryloxide and Cp groups. The

1   **2**   **3**: R = Ph   **5**
                   4: R = Me

i. 2 Bu^{n}Li

ii.

iii. H$^+$/H$_2$O

Pd/C

6

i. base

ii. Pd/C

7: R = H
8: R = Ph

BiNp$_3$Cl$_2$

tetramethylguanidine

9

9

Scheme 1

CpTiCl$_3$

ArOH/py/-pyHCl
or LiOAr/-LiCl

10a: Ar = Ph
10b: Ar = Np

11: R = Me, Ar = Ph
12a: R = Bu^t, Ar = Ph
**12b**: R = Bu^t, Ar = Np

2Na/Hg

−2NaCl

10b

13

Scheme 2

Table 1 Structural parameters for [(X)(Y)TiCl₂] and [(X)(Y)Ti(μ-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.
Cp₂TiCl₂	131	94	2.36 (av.)	—	7
CpTi(OC₆HNp₂-2,6-Buᵗ₂-3,5)₂Cl₂ **12b**	118	102	2.23 (av.)	—	This work
Ti(OC₆H₃Ph₂-2,6)₂Cl₂	109	113	2.206(1)	—	8
[Cp₂Ti(μ-Cl)]₂	133	79	2.55 (av.)	3.95 (av.)	9
[CpTi(OC₆H₂Np-2-Buᵗ₂-4,6)(μ-Cl)]₂ **13**	125	115	2.40 (av.)	3.336(1)	This work
[Ti(OC₆H₃Ph₂-2,6)₂(μ-Cl)]₂	144	102	2.37 (av.)	2.9827(7)	10
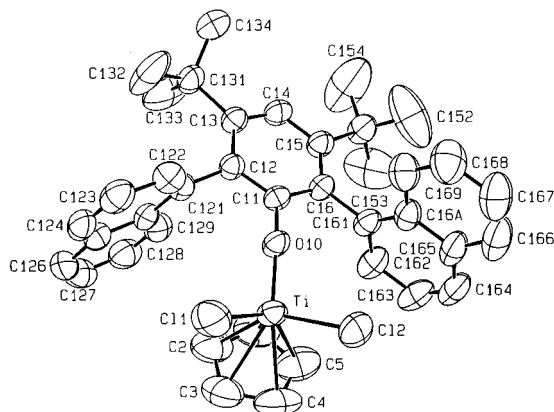
Fig. 1 Molecular structure of **12b** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–O(10) 1.774(3), Ti–Cl(1) 2.230(2), Ti–Cl(2) 2.244(2); Cl–Ti–Cl 102.36(7), Cp–Ti–O(10) 118.6(2), Ti–O(10)–C(11) 164.1(3).
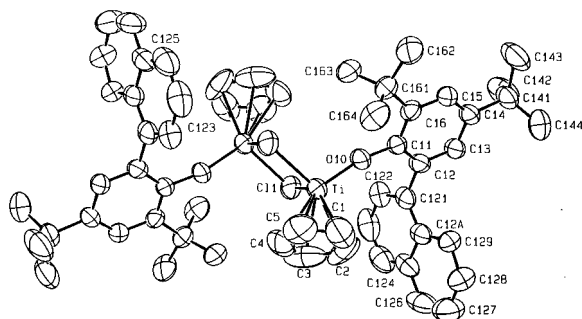
Fig. 2 Molecular structure of **13** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–Ti 3.336(1), Ti–O(10) 1.817(2), Ti–Cl(1) 2.400(1), 2.406(1); Cl(1)–Ti–Cl(1) 92.07(4), Cp–Ti–O(10) 125.1(3), Ti–O(10)–C(11) 166.7(2).

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(μ-Cl)₂Ti unit.

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, O*H*); 1.44 (s, 1.32 [s, C(C*H*₃)₃]. **7**: (CDCl₃) δ 6.80–8.20; 4.78 (s, 4.74 (s, O*H*). **8**: (CDCl₃) δ 7.00–8.10; 4.95 (s, 4.93 (s, O*H*). **9**: δ 7.9–7.23 (m); 4.15 (s, O*H*); 1.18 [s, C(C*H*₃)₃]. **10a**: δ 7.22–8.20; 5.60 (s, C₅*H*₅); 1.67 (s, 1.25 [s, C(C*H*₃)₃]. **10b**: δ 7.20–7.60; 5.70 (s, C₅*H*₅); 1.63 (s, 1.27 [s, C(C*H*₃)₃]. **11**: δ 7.19–7.36; 6.79 (s, *para*-H); 5.78 (s, C₅*H*₅); 2.03 (s, *meta*-CH₃). **12a**: δ 7.72 (s, *para*-H); 7.30–7.16 (m); 5.91 (s, C₅*H*₅); 1.23 [s, C(C*H*₃)₃]. **12b**: δ 7.87 (s, *para*-H); 7.71–7.13 (m); 5.32 (s, C₅*H*₅); 1.10 [s, C(C*H*₃)₃]. ¹³C NMR (C₆D₆, unless otherwise stated, 30 °C): **6**: (CDCl₃) δ 149.3 (O–*C*); 123.8–141.8; 35.1, 34.4 [*C*(CH₃)₃]; 31.7, 29.7 [C(*C*H₃)₃]. **7**: (CDCl₃) δ 150.7, 150.6 (*C*O); 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 (*C*O); 136.4, 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(*C*H₃)₃]. **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(*C*H₃)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 (*C*₅H₅); 35.9, 34.7 [*C*(CH₃)₃]; 31.5, 30.6 [C(*C*H₃)₃]. **11**: δ 164.3 (Ti–O–*C*); 120.2 (*C*₅H₅); 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 (*C*₅H₅); 37.5 [*C*(CH₃)₃]; 33.0 [C(*C*H₃)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 (*C*₅H₅); 37.9 [*C*(CH₃)₃]; 32.8 [C(*C*H₃)₃].

‡ *Crystal data*: for **12b** at 296 K: TiCl₂OC₃₉H₃₈, *M* = 641.54, space group P̄1 (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*꜀ = 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*ₒ² > 2σ(*F*ₒ²) were used in the final least-squares refinement to yield *R*(*F*ₒ) = 0.076 and *R*ᵥᵥ(*F*ₒ²) = 0.190. For **13** at 296 K: Ti₂Cl₂O₂C₅₈H₆₄, *M* = 959.86, space group P2₁/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*꜀ = 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*ₒ² > 2σ(*F*ₒ²) were used in the final least-squares refinement to yield *R*(*F*ₒ) = 0.074 and *R*ᵥᵥ(*F*ₒ²) = 0.169.

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