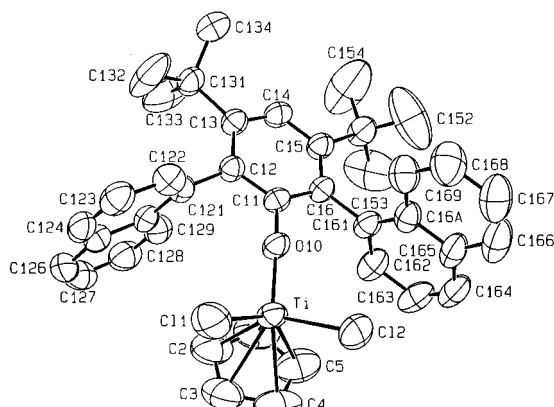
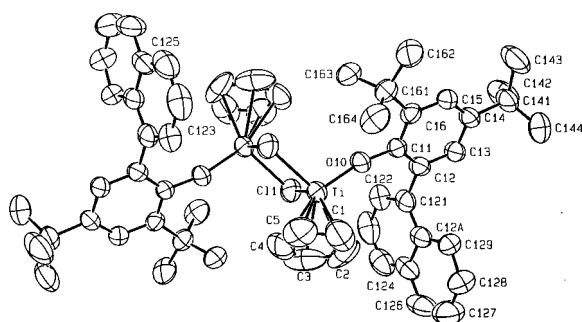


Table 1 Structural parameters for [(X)(Y)TiCl₂] and [(X)(Y)Ti(μ-Cl)₂Ti(X)(Y)]; X, Y = Cp or ArO (Np = 1-naphthyl)

Compound	X–Ti–Y ^o	Cl–Ti–Cl ^o	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 -3,5) ₂ Cl ₂ 12b	118	102	2.23 (av.)	—	This work
Ti(OC ₆ H ₃ Ph ₂ -2,6) ₂ Cl ₂	109	113	2.206(1)	—	8
[Cp ₂ Ti(μ-Cl)] ₂	133	79	2.55 (av.)	3.95 (av.)	9
[CpTi(OC ₆ H ₃ Np-2-Bu ^t -4,6)(μ-Cl)] ₂ 13	125	115	2.40 (av.)	3.336(1)	This work
[Ti(OC ₆ H ₃ Ph ₂ -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.

We thank the National Science Foundation (Grant CHE-9321906) for financial support of this research.

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) δ 7.00–8.10; 4.95 (s), 4.93 (s, OH). **9**: δ 7.9–7.23 (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**: δ 7.20–7.60; 5.70 (s, C₅H₅); 1.63 (s), 1.27 [s, C(CH₃)₃]. **11**: δ 7.19–7.36; 6.79 (s, *para*-H); 5.78 (s, C₅H₅); 2.03 (s, *meta*-CH₃). **12a**: δ 7.72 (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 (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(CH₃)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 (C₅H₅); 36.0, 34.7 [C(CH₃)₃]; 31.5, 30.7 [C(CH₃)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(CH₃)₃]; 33.0 [C(CH₃)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 *P1* (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*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.076 and *R*_w(*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*_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*_o² > 2σ(*F*_o²) were used in the final least-squares refinement to yield *R*(*F*_o) = 0.074 and *R*_w(*F*_o²) = 0.169.

- S. Saito and H. Yamamoto, *Chem. Commun.*, 1997, 1585.
- I. P. Rothwell, *Chem. Commun.*, 1997, 1331; *Acc. Chem. Res.*, 1988, **21**, 153.
- D. L. Clark, G. B. Deacon, T. Feng, R. V. Hollis, B. L. Scott, B. W. Skelton, J. G. Watkin and A. H. White, *Chem. Commun.*, 1996, 1729 and references therein.
- J. S. Vilaro, M. A. Lockwood, L. G. Hanson, J. R. Clark, B. C. Parkin, P. E. Fanwick and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, 1997, 3353.
- For related *ortho*-(2-alkylphenyl)phenols see S. Saito, T. Kano, K. Hatanaka and H. Yamamoto, *J. Org. Chem.*, 1997, **62**, 5651.
- D. H. R. Barton, D. M. X. Donnelly, P. J. Guiry and J. H. Reibenspies, *J. Chem. Soc., Chem. Commun.*, 1990, 1110; D. H. R. Barton, N. Y. Bhatnagar, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, D. J. Lester, W. B. Motherwell, M. T. B. Papoula and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2657.
- A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina and R. Ropal, *Can. J. Chem.*, 1975, **53**, 1622.
- J. R. Dilworth, J. Hanich, M. Krestel, J. Beck and J. Strahle, *J. Organomet. Chem.*, 1986, **315**, C9.
- R. Jungst, D. Sekutowski, J. Davis, M. Luly and G. Stucky, *Inorg. Chem.*, 1977, **7**, 1645.
- J. E. Hill, P. E. Fenwick and I. P. Rothwell, *Polyhedron*, 1990, **9**, 1617.

Communication 8/05034A