

## Facile resolution of constrained geometry indenyl-phenoxide ligation†

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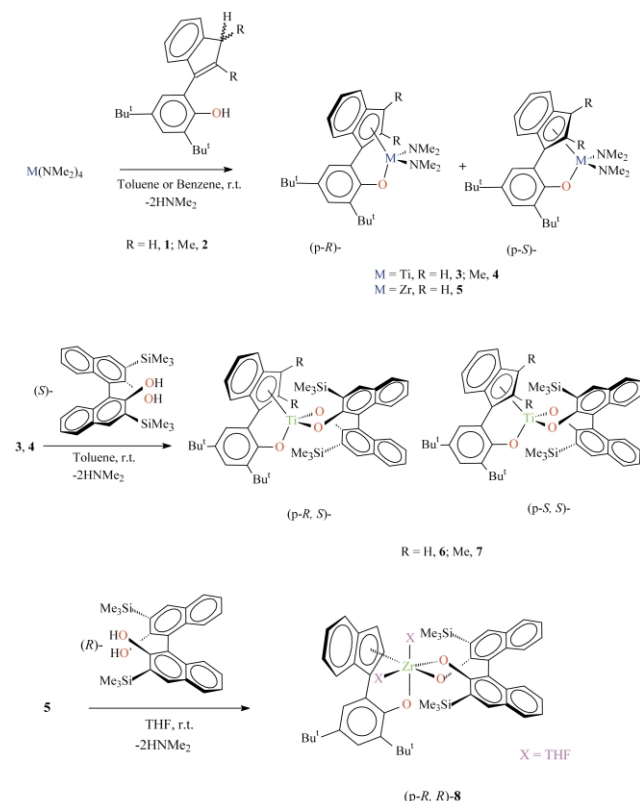
The 2-(inden-3-yl)phenoxide ligand can be resolved at both tetrahedral and octahedral Group 4 metal centers using chiral binaphthoxide ligands.

The chemistry of ansa metallocenes and constrained geometry ligands at Group 4 metal centers continues to be an important area of transition metal chemistry.<sup>1</sup> Of particular interest has been the design and application of chiral ligands of this type.<sup>2</sup> We have begun to study the coordination chemistry of 2-(indenyl)phenoxide ligands, which demonstrate a variety of coordination modes.<sup>3</sup> We wish to report here the resolution of this ligand system at both tetrahedral and an unusual octahedral Group 4 metal center.

Hydrocarbon solution of the ligands **1** and **2** (1 equiv.) react with the substrates  $[M(NMe_2)_4]$  ( $M = Ti, Zr$ )<sup>4</sup> to produce the corresponding bis(amides) **3–5** via activation of both the phenolic OH and indenyl CH bonds (Scheme).†‡ Structural studies of **3–5**,§ show the presence of both the (*p-R*) and (*p-S*) enantiomers within the unit cell due to the planar chirality generated via the indenyl coordination; Figure 1 shows (*p-R*)-**3**.

The remaining dimethylamido ligands in **3–5** can undergo protonolysis reactions with a variety of reagents. Reaction of the Ti compounds **3** or **4** with (*S*)-3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diol in aromatic solvents was found to initially produce a mixture of two diastereoisomers (**6** and **7**, Scheme 1) with well-resolved ligand signals within the NMR spectra. However, although at low temperatures a 50/50 mixture of isomers was observed for **6**, at ambient temperature the formation of a major isomer was found to take place. Isolated crystals from this reaction mixture were found to contain only one diastereoisomer, the thermodynamically more stable (*p-S,S*) form of **6**. The presence of the methyl substituents on the indenyl ring of **7** does not appear to allow isomerization and a 50/50 mixture is maintained even at 100 °C for days. Crystallization, however, did lead to the pure (*p-S,S*) form of **7** (Figure 2). In previous studies of pseudo-tetrahedral *rac*-bis(indenyl) ligand systems it has been shown that (*S*)-binaphthoxide ligands lead to a preferential (*p-S*) coordination of the indenyl rings.<sup>5</sup> The change in chirality of the chelated indenyl-phenoxide ligand cannot occur via simple phenoxide dissociation. Instead “flipping” of the indenyl ring must occur. We believe this occurs via a reversal of the process that leads to **3** and **4**. Specifically it seems reasonable to propose reversible protonation of the indenyl ring can occur by the dimethylamine generated within the reaction. There is precedence for such a process in the interconversion of *mer*- and *rac*-bis(indenyl) systems.<sup>6</sup> In the case of the 2,3-dimethyl-indenyl ligand, however, this process cannot lead directly to ring-flipping as the proton has to be abstracted from the same face to which it was originally delivered.

The reaction of **5** with (*R*)-3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diol also gave an initial 50/50 mixture of



Scheme 1 Synthesis of compounds.

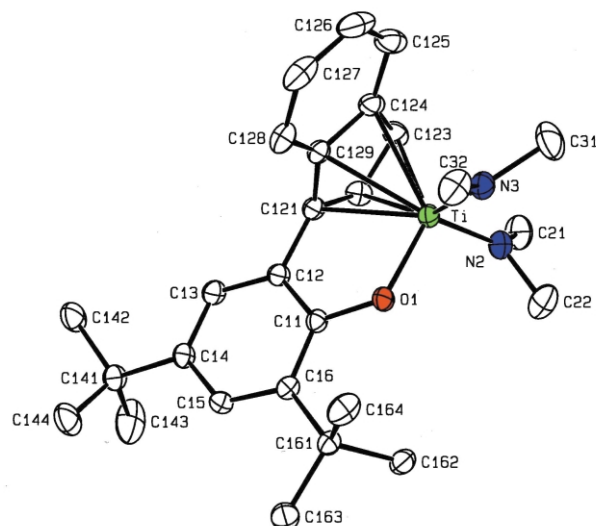
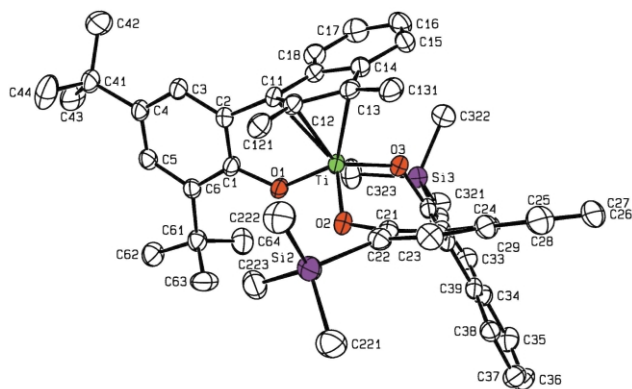
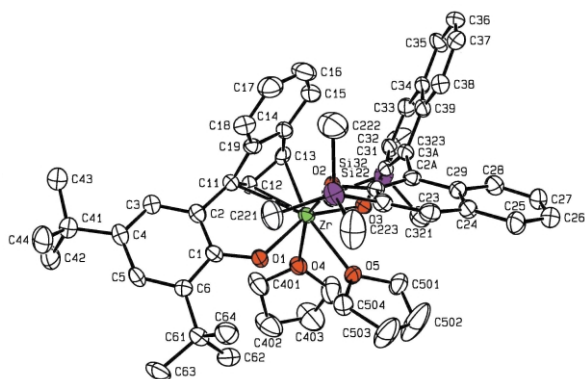


Fig. 1 Selected bond distances (Å) and angles (°) for **3**; (*p-R* form shown) Ti–O(1) 1.895(1), Ti–N(2) 1.905(2), Ti–N(3) 1.913(2), Ti–C(121) 2.366(2), Ti–C(122) 2.381(2), Ti–C(123) 2.380(2), Ti–C(124) 2.417(2), Ti–C(129) 2.405(2), O(1)–Ti–N(2) 107.07(6), O(1)–Ti–N(3) 100.22(6), N(2)–Ti–N(3) 102.02(6).

† Electronic supplementary information (ESI) available: synthesis of compounds **1–8** and ORTEP views of **4,5** and **6**. See <http://www.rsc.org/suppdata/cc/b2/b212724e/>



**Fig. 2** Selected bond distances (Å) and angles (°) for (p-*S,S*)-**7**: Ti–O(1) 1.864(2), Ti–O(2) 1.862(2), Ti–O(3) 1.866(2), Ti–C(11) 2.310(3), Ti–C(12) 2.318(3), Ti–C(13) 2.361(3), Ti–C(14) 2.522(3), Ti–C(19) 2.472(3), O(1)–Ti–O(2) 96.91(9), O(2)–Ti–O(3) 102.09(9), O(1)–Ti–O(3) 115.72(9).



**Fig. 3** Selected bond distances (Å) and angles (°) for (p-*R,R*)-**8**: Zr–O(1) 2.100(3), Zr–O(2) 2.017(3), Zr–O(3) 2.095(3), Zr–O(4) 2.387(3), Zr–O(5) 2.356(3), Zr–C(11) 2.531(4), Zr–C(12) 2.511(4), Zr–C(13) 2.564(4), Zr–C(14) 2.723(4), Zr–C(19) 2.696(4), O(1)–Zr–O(2) 99.1(1), O(2)–Zr–O(3) 92.6(1), O(1)–Zr–O(3) 150.5(1), O(2)–Zr–O(5) 82.25(12), O(3)–Zr–O(5) 76.0(1), O(1)–Zr–O(5) 78.8(1), O(2)–Zr–O(4) 159.0(1), O(3)–Zr–O(4) 79.2(1), O(1)–Zr–O(4) 80.3(1), O(5)–Zr–O(4) 77.1(1).

diastereoisomers. It has proven difficult to isolate crystalline products from hydrocarbon solvents. However, use of THF was found to lead to crystals of a new compound **8** shown to contain a pseudo-octahedral zirconium metal center (Figure 3). Interestingly **8** can be seen to contain a p-*R* chelated indenylphenoxide and two, cis-coordinated THF molecules along with the (*R*)-binol ligand. It is also important to note that the indenyl ring is only  $\eta^3$ -bound in the solid state of **8**, with significant elongation of the Zr–C(aromatic) distances (Figure 3). A similar bonding mode is also seen in **7** (Figure 2) whereas the indenyl ring in **3** (Figure 1) more closely approaches  $\eta^5$ -coordination.

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## Notes and references

† Selected spectroscopic data. For **3**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  6.75–7.61 (aromatics); 6.43, 6.33 (d,  $\eta^5\text{-CH}$ ); 3.27, 2.49 (s,  $\text{NMe}_2$ ); 1.68, 1.44 (s,  $\text{CMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  172.5 (Ti–O–C); 101.3 ( $\eta^5\text{-CH}$ ). For **4**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  6.81–7.60 (aromatics); 3.11, 2.59 (s,  $\text{NMe}_2$ ); 2.22, 1.99 (s,  $\text{CH}_3$ ); 1.65, 1.44 (s,  $\text{CMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  172.2 (Ti–O–C); 108.1 ( $\eta^5\text{-CMe}$ ). For **5**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$

6.85–7.59 (aromatics); 6.55, 6.19 (d,  $\eta^5\text{-CH}$ ); 2.91, 2.31 (s,  $\text{NMe}_2$ ); 1.64, 1.44 (s,  $\text{CMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  171.0 (Zr–O–C); 95.5 ( $\eta^5\text{-CH}$ ). For **6** (p-*S,S*):  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  6.65–8.25 (aromatics); 5.44 (d,  $\eta^5\text{-CH}$ ); 1.35, 1.32 (s,  $\text{CMe}_3$ ); 0.42, 0.29 (s,  $\text{SiMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  173.1, 165.6, 156.6 (Ti–O–C); 106.3 ( $\eta^5\text{-CH}$ ). For **7** (p-*S,S*):  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  6.49–8.16 (aromatics); 2.27, 1.62 (s,  $\text{CH}_3$ ); 1.35, 1.22 (s,  $\text{CMe}_3$ ); 0.49, 0.28 (s,  $\text{SiMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  173.2, 163.8, 160.7 (Ti–O–C); 100.3 ( $\eta^5\text{-CMe}$ ). (p-*R,S*):  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  5.81–7.96 (aromatics); 2.24, 1.59 (s,  $\text{CH}_3$ ); 1.47, 1.33 (s,  $\text{CMe}_3$ ); 0.46, 0.16 (s,  $\text{SiMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  173.0, 168.7, 156.9 (Ti–O–C); 108.1 ( $\eta^5\text{-CMe}$ ). For **8** (p-*R,R*):  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  6.53–8.28, (aromatics); 5.59 (s,  $\eta^5\text{-CH}$ ); 3.57 (s, O– $\text{CH}_2\text{-CH}_2$ ); 1.39 (s, O– $\text{CH}_2\text{-CH}_2$ ); 1.35, 1.26 (s,  $\text{CH}_3$ ); 1.35 (s), 1.22 (s,  $\text{CMe}_3$ ); 0.49 (s), 0.36 (s,  $\text{SiMe}_3$ ). Selected  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  171.9, 160.7 (Zr–O–C); 99.4 ( $\eta^5\text{-CH}$ ).

‡ Crystal data: For **3** at 150 K:  $\text{C}_{27}\text{H}_{38}\text{N}_2\text{OTi}$ ,  $M = 454.52$ , space group  $P2_1/n$  (No. 14),  $a = 12.4594(3)$ ,  $b = 11.7575(3)$ ,  $c = 18.0226(4)$  Å,  $\beta = 108.1734(13)^\circ$ ,  $V = 2508.5(2)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.203$  g cm<sup>-3</sup>,  $Z = 4$ . Of the 5700 unique reflections collected ( $5 \leq \theta \leq 27^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 5694 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.041$  and  $R_w = 0.099$ . For **4** at 150 K:  $\text{C}_{29}\text{H}_{42}\text{N}_2\text{OTi}$ ,  $M = 482.57$ , space group  $P2_1/c$  (No. 14),  $a = 10.0202(2)$ ,  $b = 13.0802(3)$ ,  $c = 22.0926(4)$  Å,  $\beta = 102.3111(13)^\circ$ ,  $V = 2829.01(19)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.133$  g cm<sup>-3</sup>,  $Z = 4$ . Of the 6044 unique reflection collected ( $5 \leq \theta \leq 27^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 6040 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.061$  and  $R_w = 0.160$ . For **5** at 150 K:  $\text{C}_{27}\text{H}_{38}\text{N}_2\text{OZr}$ ,  $M = 497.84$ , space group  $P1$  (No. 2),  $a = 12.9534(3)$ ,  $b = 14.0719(4)$ ,  $c = 15.2631(4)$  Å,  $V = 2589.5(2)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.277$  g cm<sup>-3</sup>,  $Z = 4$ . Of the 11660 unique reflections collected ( $5 \leq \theta \leq 27^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 9145 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.053$  and  $R_w = 0.136$ . For **6** at 150 K:  $\text{C}_{49}\text{H}_{54}\text{O}_3\text{Si}_2\text{Ti}$ ,  $M = 795.05$ , space group  $P2_1$  (No. 4),  $a = 11.9436(10)$ ,  $b = 13.1268(10)$ ,  $c = 16.1538(12)$  Å,  $\beta = 102.861(4)^\circ$ ,  $V = 2469.1(6)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.069$  g cm<sup>-3</sup>,  $Z = 2$ . Of the 7600 unique reflections collected ( $5 \leq \theta \leq 25^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 7586 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.087$  and  $R_w = 0.187$ . For **7** at 150 K:  $\text{C}_{49}\text{H}_{54}\text{O}_3\text{Si}_2\text{Ti}$ ,  $M = 823.10$ , space group  $P2_1$  (No. 4),  $a = 12.0012(4)$ ,  $b = 13.6234(5)$ ,  $c = 16.3611(6)$  Å,  $\beta = 105.5417(14)^\circ$ ,  $V = 2577.2(3)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.061$  g cm<sup>-3</sup>,  $Z = 2$ . Of the 10232 unique reflection collected ( $5 \leq \theta \leq 30^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 10199 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.053$  and  $R_w = 0.148$ . For **8**  $\text{C}_68\text{H}_{86}\text{O}_6\text{Si}_2\text{Zr}$ ,  $M = 1146.83$ , space group  $P2_12_12_1$  (No. 19),  $a = 12.5231(3)$ ,  $b = 19.2231(4)$ ,  $c = 25.9127(6)$  Å,  $V = 2964.61(10)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.221$  g cm<sup>-3</sup>,  $Z = 4$ . Of the 12567 unique reflections collected ( $5 \leq \theta \leq 26^\circ$ ) with  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073$  Å), the 12553 with  $F_o^2 > 2.0 \sigma(F_o^2)$  were used in the final least-squares refinement to yield  $R = 0.063$  and  $R_w = 0.136$ . Flack parameters: compound **6**, 0.04(5); compound **7**, -0.01(2); compound **8**, 0.03(4). CCDC 201167–201170, 201172, 201174. See <http://www.rsc.org/suppdata/cc/b2/b212724e/> for crystallographic data in .cif or other electronic format.

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