

Coordination modes of 2-(indenyl)phenoxide ligation at early d-block metal centers

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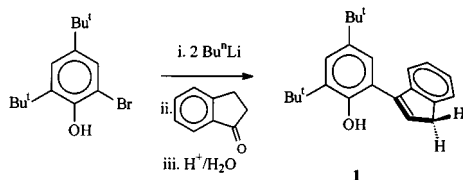
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Three distinct bonding modes for the ligand 2-(indenyl)-4,6-di-*tert*-butylphenoxide at early d-block metal centers have been identified

The use of constrained geometry cyclopentadienyl ligation has had a considerable impact on early transition metal chemistry in recent years.¹ As part of our work on novel *ortho*-substituted aryloxy ligation² we have synthesized the compound 2-(inden-3-yl)-4,6-di-*tert*-butylphenol **1** (Scheme 1).³ Unlike previously reported ligands of this type, chelation of **1** to a metal center *via* deprotonation will generate an inherently chiral environment. Here we report on our initial forays into the chemistry of this ligand, which demonstrate three distinct bonding modes to transition metal centers.



Scheme 1

Compound **1** is obtained in gram quantities *via* the synthetic route shown in Scheme 1. When **1** is added to the compound [CpTiCl₃] in the presence of excess pyridine the simple aryloxy [Cp₂Ti(OC₆H₃Bu^t₂-4,6-Ind-2)Cl₂] **2** is obtained.[†] The solid state structure of **2** (Fig. 1) shows the *ortho*-inden-3-yl group to be unbound with a Ti–O–C angle of 158.7(1)°.‡ Surprisingly, addition of LiMe to **2** produces the corresponding dimethyl derivative **3** (Scheme 2) with no deprotonation of the inden-3-yl ligand being observed. At ambient temperatures the potentially diastereotopic methylene protons in the *ortho*-inden-3-yl groups of both **1** and **2** appear as broad singlets in the ¹H NMR spectra owing to inden-3-yl rotation on the NMR timescale. At lower temperatures these signals broaden and resolve into the AB pattern expected for the static structure. Similarly both Ti–Me groups in **3** appear as one broad singlet in

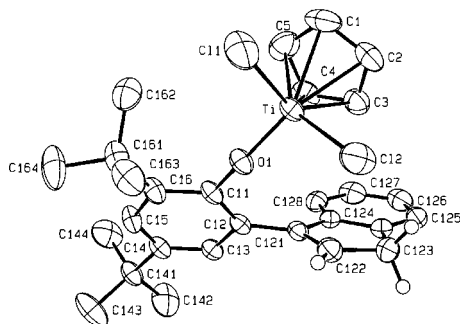
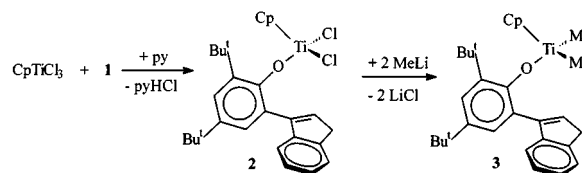


Fig. 1 Molecular structure of **2** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–O(1) 1.785(2), Ti–Cl(1) 2.2581(8), Ti–Cl(2) 2.2554(8); Cl–Ti–Cl 100.24(4), Cp–Ti–O(1) 118.1(1), Ti–O(1)–C(11) 158.7(1).

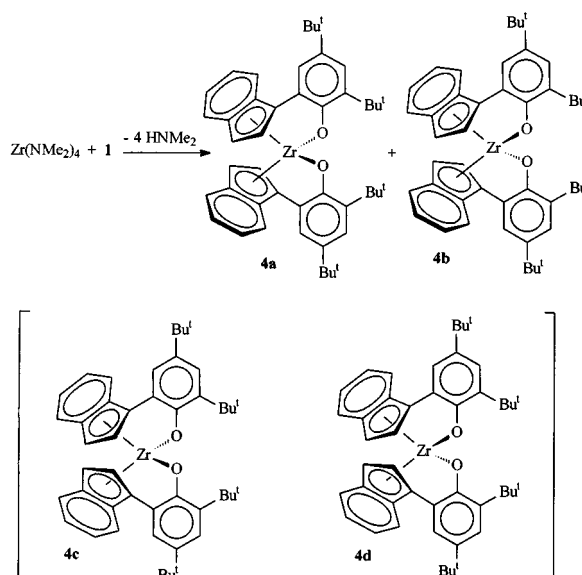


Scheme 2

both the ¹H and ¹³C NMR spectra at ambient temperatures but appear as two well resolved resonances at lower temperatures. Variable temperature NMR studies of **2** and **3** in toluene-*d*₈ allow the barrier to inden-3-yl rotation (enantiomer inter-conversion) to be estimated at 13.9(5) kcal mol^{−1} (at 20 °C) and 13.4(5) kcal mol^{−1} (at −5 °C), respectively. These barriers are significantly lower than that measured for corresponding 2-(1-naphthyl)phenoxides.^{2c}

Addition of **1** to the zirconium precursor [Zr(NMe₂)₄]⁴ leads to the complex [Zr{(OC₆H₃Bu^t₂-4,6-(η^5 -Ind))₂] **4**. In solution **4** is shown by NMR to exist as a mixture of two isomers (Scheme 3). Recrystallization from benzene–pentane generates crystals of **4a** shown (Fig. 2) to contain a crystallographic C₂ axis of symmetry. It can be seen that in the solid state both indenyl rings are η^5 -bound to the same zirconium metal center, Zr–O–C angle = 128.4(2)°. In CDCl₃ solution **4a** undergoes slow (days at room temperature) conversion to a 50:50 mixture of **4a**:**4b**. In both **4a** and **4b** the aryloxy groups are equivalent (NMR) ruling out their formulation as the two alternative isomers **4c** and **4d** that contain no symmetry elements (Scheme 3).

Treatment of the compound [Ta(NMe₂)₅]⁵ with **1** initially produces the substitution compound **5** (Scheme 4) with elimination of one equivalent of HNMe₂. Upon thermolysis



Scheme 3

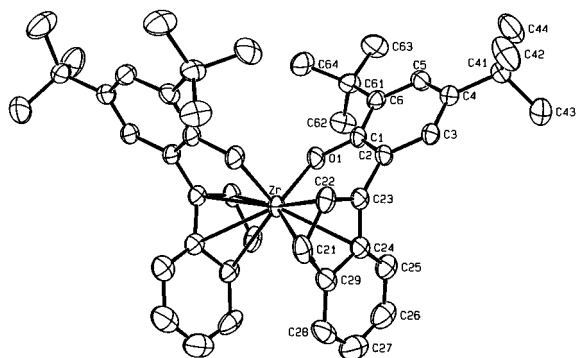
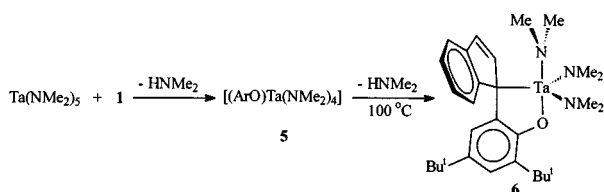


Fig. 2 Molecular structure of **4a** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Zr–O(1) 2.015(2), Zr–C(23) 2.487(3), Zr–C(22) 2.500(3), Zr–C(21) 2.532(3), Zr–C(24) 2.568(3), Zr–C(29) 2.640(3), O(1)–Zr–O(1) 97.6(1), Zr–O(1)–C(1) 128.4(2).



Scheme 4

(100 °C) in C_6D_6 , a further equivalent of $HNMe_2$ is lost from **5** with formation of **6** (Scheme 4). The solid state structure of **6** (Fig. 3) shows the ligand to be chelated to the metal *via* an η^1 -indenyl interaction, Ta–O–C angle = 122.7(6)°. The metal is attached to the *ipso* carbon atom yielding a five-membered metallacycle ring. The coordination environment about the Ta metal center in **6** is best described as *tbp*, with an axial oxygen atom. In the ambient temperature 1H NMR spectrum of **6** a single broad resonance is observed for the Ta– NMe_2 protons. At lower temperatures this signal splits out into four singlets in the ratio of 2:2:1:1. We interpret the two larger signals as being due to the two, non-equivalent equatorial Ta– NMe_2 groups undergoing rapid rotation. The remaining signals are due to the unique axial Ta– NMe_2 group that is undergoing restricted rotation on the NMR timescale. Presumably the higher barrier to rotation of the axial group is due to the presence of the η^1 -indenyl ring (Fig. 3).

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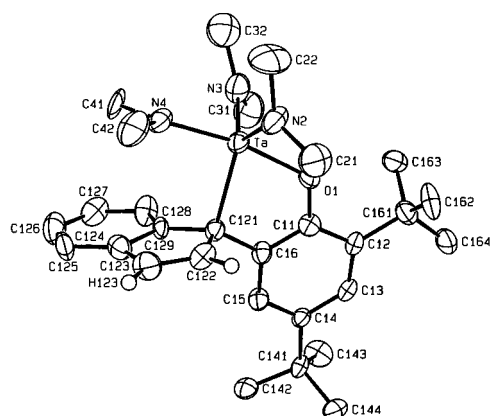


Fig. 3 Molecular structure of **6** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–N(2) 1.95(1), Ta–N(3) 1.95(1), Ta–N(4) 2.005(8), Ta–C(121) 2.285(9), Ta–O(1) 2.025(7); O(1)–Ta–N(4) 169.9(3), O(1)–Ta–N(2) 90.8(3), O(1)–Ta–N(3) 93.8(4), O(1)–Ta–C(121) 75.4(3), N(2)–Ta–N(3) 117.6(5), N(2)–Ta–N(4) 92.8(4), N(3)–Ta–N(4) 92.9(4), C(121)–Ta–N(2) 123.6(4), C(121)–Ta–N(3) 117.7(4), C(121)–Ta–N(4) 94.7(3), Ta–O(1)–C(11) 122.7(6).

Notes and references

† Spectral data obtained in C_6D_6 at 30 °C unless otherwise stated. 1H NMR: **1**: ($CDCl_3$) δ 7.27–7.67 (aromatics); 6.78 (t, 3J 2.1 Hz, CH); 5.68 (s, OH); 3.69 (d, 3J 1.6 Hz, CH_2); 1.57 (s), 1.44 [s, $C(CH_3)_3$]. **2**: δ 7.13–7.61 (aromatics); 6.61 (t, CH); 5.81 (s, C_5H_5); 3.36 (br, CH_2); 1.61 (s), 1.28 [s, $C(CH_3)_3$]. (C_7D_8 , –30 °C): δ 6.72–7.58 (aromatics); 6.60 (br, CH); 5.67 (s, C_5H_5); 3.48 (d), 3.12 (d, 2J 23.8 Hz, CH_2); 1.58 (s), 1.25 [s, $C(CH_3)_3$]. **3**: δ 7.57 (d), 7.33 (d, 4J 2.4 Hz, mC_6H_2); 7.04–7.55 (other aromatics); 6.29 (t, CH); 5.59 (s, C_5H_5); 3.05 (d, CH_2); 1.60 (s), 1.28 [s, $C(CH_3)_3$]; 0.64 (br, TiMe). (C_7D_8 , –45 °C): δ 6.97–7.61 (aromatics); 6.31 (d, CH); 5.50 (s, C_5H_5); 2.99 (AB, CH_2); 1.64 (s), 1.30 [s, $C(CH_3)_3$]; 0.76 (s), 0.65 (s, TiMe). **4**: δ 6.79–7.40 (aromatics); 6.18 (d), 6.12 (d), 5.19 (d, η^5 - C_5H_2); 1.36 (s), 1.29 (s), 1.29 (s), 1.24 [s, $C(CH_3)_3$]. ($CDCl_3$): δ 6.89–7.48 (aromatics); 6.89 (d), 6.75 (d), 6.62 (d), 5.42 (d, η^5 - C_5H_2); 1.31 (s), 1.30 (s), 1.19 (s), 1.05 [s, $C(CH_3)_3$]. **5**: δ 7.17–7.73 (aromatics); 6.60 (t, CH); 3.48 (br, CH_2); 3.15 (s, NMe_2); 1.70 (s), 1.37 [s, $C(CH_3)_3$]. **6**: δ 7.58 (d), 7.51 (d), 7.28 (t), 7.05 (t, C_6H_4); 7.43 (d), 6.76 (d, *m*-H); 7.10 (d), 6.62 (d, C_5H_2); 2.76 (br, NMe_2); 1.74 (s), 1.15 [s, $C(CH_3)_3$]. (C_7D_8 , 40 °C): δ 7.56 (d), 7.49 (d), 7.25 (t), 7.05 (t, C_6H_4); 7.39 (d), 6.69 [d, 4J 1.7 Hz, *m*-H]; 7.09 (d), 6.64 (d, C_5H_2); 2.87 (s, NMe_2); 1.73 (s), 1.21 [s, $C(CH_3)_3$]. (C_7D_8 , –30 °C): δ 6.59–7.63 (aromatics); 2.98 (br), 2.43 (br), 1.92 (br, NMe_2); 1.79 (s), 1.18 [s, $C(CH_3)_3$]. (C_7D_8 , –55 °C): δ 6.57–7.64 (aromatics); 3.00 (s, 6H), 2.86 (s, 6H), 2.36 (s, 3H), 1.88 (s, 3H, NMe_2); 1.81 (s), 1.17 [s, $C(CH_3)_3$]. Selected ^{13}C NMR, **1**: ($CDCl_3$): δ 149.3 (OC); 144.4, 144.2, 141.7, 141.5, 135.3, 132.7, 126.5, 125.5, 124.1, 123.9, 123.8, 121.2, 120.9 (unsaturated C); 38.7 (CH_2); 35.1, 34.3 [$C(CH_3)_3$]; 31.7, 29.7 [$C(CH_3)_3$]. **2**: δ 165.5 (TiOC); 121.0 (C_5H_5); 38.7 (CH_2); 35.9, 34.7 [$C(CH_3)_3$]; 31.5, 30.6 [$C(CH_3)_3$]. **3**: δ 161.7 (TiOC); 114.3 (C_5H_5); 57.7 (br, TiMe); 38.4 (CH_2); 35.7, 34.5 [$C(CH_3)_3$]; 31.7, 30.5 [$C(CH_3)_3$]. (C_7D_8 , –45 °C): δ 161.6 (TiOC); 114.3 (C_5H_5); 58.8, 56.8 (TiMe); 38.3 (CH_2); 35.8, 34.6 [$C(CH_3)_3$]; 31.7, 30.3 [$C(CH_3)_3$]. **4**: δ 172.2, 171.5 (ZrOC); 115.5, 97.0, 96.9 (η^5 - C_5H_2); 35.1, 34.5, 34.4 [$C(CH_3)_3$]; 31.9, 29.6 [$C(CH_3)_3$]. ($CDCl_3$, 30 °C): δ 171.5, 170.9 (ZrOC); 115.2, 99.9, 96.6, 96.4 (η^5 - C_5H_2); 34.7, 34.3, 34.2, 34.1 [$C(CH_3)_3$]; 31.8, 31.8, 30.2, 29.2 [$C(CH_3)_3$]. **5**: δ 157.2 (TaOC); 47.1 (NMe_2); 39.1 (CH_2); 35.8, 34.5 [$C(CH_3)_3$]; 31.8, 30.3 [$C(CH_3)_3$]. **6**: δ 163.0 (TaOC); 103.4 (TaC); 44.5 (NMe_2); 35.1, 34.5 [$C(CH_3)_3$]; 32.0, 30.4 [$C(CH_3)_3$].

‡ Crystallographic data: for **2** at 203 K: $TiOCl_2C_{31}H_{35}$, $M = 542.43$, space group $P2_1/n$ (no. 14), $a = 12.2422(4)$, $b = 12.6093(4)$, $c = 18.9505(6)$ Å, $\beta = 102.517(2)^\circ$, $V = 2855.8(3)$ Å³, $D_c = 1.262$ g cm^{–3}, $Z = 4$. Of the 5004 unique reflections collected ($8.00 \leq 2\theta \leq 60.94^\circ$) with Mo- K_α ($\lambda = 0.71073$ Å), the 4070 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.045$ and $R_w(F_o^2) = 0.111$; for **4a** at 203 K: $ZrO_2C_{52}H_{58}$, $M = 806.26$, space group $C2/c$ (No. 15), $a = 14.3043(4)$, $b = 10.7900(5)$, $c = 28.522(1)$ Å, $\beta = 97.875(3)^\circ$, $V = 4360.7(5)$ Å³, $D_c = 1.228$ g cm^{–3}, $Z = 4$. Of the 4399 unique reflections collected ($8.00 \leq 2\theta \leq 52.73^\circ$) with Mo- K_α ($\lambda = 0.71073$ Å), 3651 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.055$ and $R_w(F_o^2) = 0.132$; for **5** at 203 K: $TaON_3C_{29}H_{44}$, $M = 631.64$, space group $P1$ (no. 2), $a = 9.6679(5)$, $b = 12.1261(6)$, $c = 13.9575(4)$ Å, $\alpha = 86.118(3)^\circ$, $\beta = 72.704(3)^\circ$, $\gamma = 67.257(2)^\circ$, $V = 1438.8(2)$ Å³, $D_c = 1.458$ g cm^{–3}, $Z = 2$. Of the 5428 unique reflections collected ($8.00 \leq 2\theta \leq 52.75^\circ$) with Mo- K_α ($\lambda = 0.71073$ Å), 5011 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o) = 0.061$ and $R_w(F_o^2) = 0.153$. Atom C(32) was refined isotropically. CCDC 182/1465.

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