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

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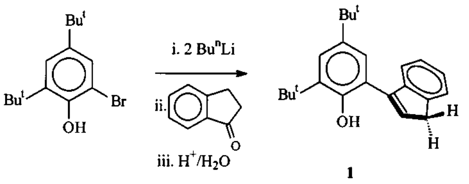
Three distinct bonding modes for the ligand 2-(indenyl)-4,6-di-*tert*-butylphenoxide at early d-block metal centers have been identified

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 aryloxide ligation[2] 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 $[CpTiCl_3]$ in the presence of excess pyridine the simple aryloxide $[Cp_2Ti(OC_6H_2Bu^t{}_2\text{-}4,6\text{-Ind-}2)Cl_2]$ **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 both the ^1H and ^{13}C 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 interconversion) 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]

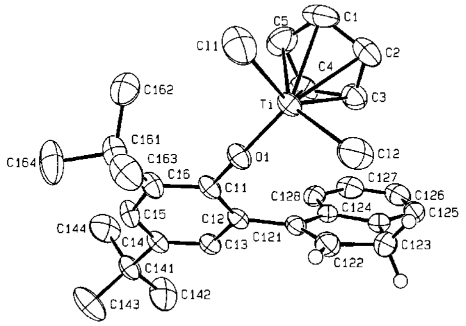
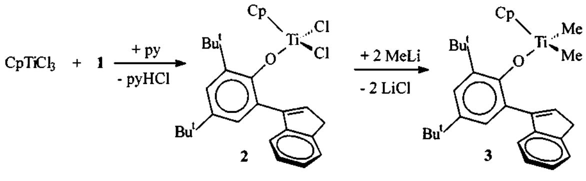


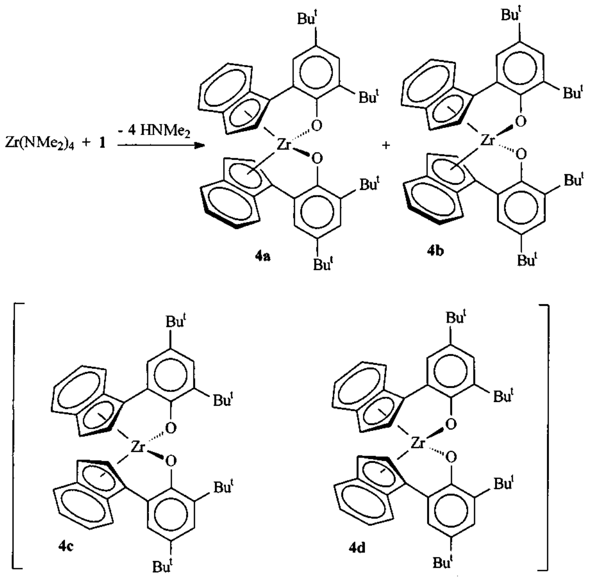
Fig. 1 Molecular structure of **2** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–O(1) 1.785(2), Ti–Cl(1) 2.2581(8), Ti–Cl(2) 2.2554(8); Cl–Ti–Cl 100.24(4), Cp–Ti–O(1) 118.1(1), Ti–O(1)–C(11) 158.7(1).



Scheme 2

Addition of **1** to the zirconium precursor $[Zr(NMe_2)_4]$[4] leads to the complex $[Zr\{(OC_6H_3Bu^t{}_2\text{-}4,6\text{-}(\eta^5\text{-Ind})\}_2]$ **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 C_2 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 $CDCl_3$ solution **4a** undergoes slow (days at room temperature) conversion to a 50 : 50 mixture of **4a** : **4b**. In both **4a** and **4b** the aryloxide 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 $[Ta(NMe_2)_5]$[5] with **1** initially produces the substitution compound **5** (Scheme 4) with elimination of one equivalent of $HNMe_2$. Upon theromolysis



Scheme 3

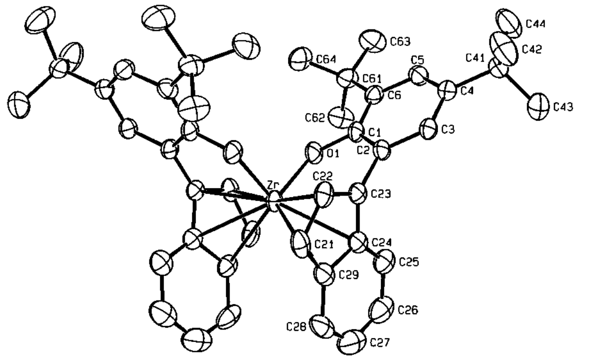
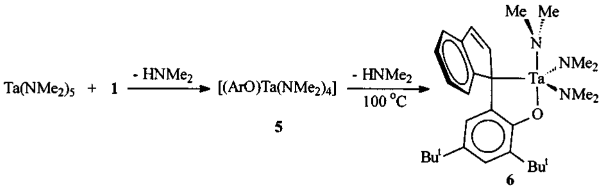


Fig. 2 Molecular structure of **4a** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Zr–O(1) 2.015(2), Zr–C(23) 2.487(3), Zr–C(22) 2.500(3), Zr–C(21) 2.532(3), Zr–C(24) 2.568(3), Zr–C(29) 2.640(3), O(1)–Zr-O(1) 97.6(1), Zr–O(1)–C(1) 128.4(2).



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 ^{1}H NMR spectrum of **6** a single broad resonance is observed for the Ta–N*Me*$_2$ 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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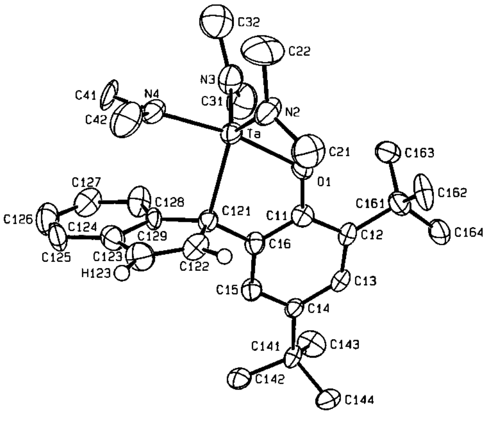

Fig. 3 Molecular structure of **6** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ta–N(2) 1.95(1), Ta–N(3) 1.95(1), Ta–N(4) 2.005(8), Ta–C(121) 2.285(9), Ta–O(1) 2.025(7); O(1)–Ta–N(4) 169.9(3), O(1)–Ta–N(2) 90.8(3), O(1)–Ta–N(3) 93.8(4), O(1)–Ta–C(121) 75.4(3), 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. ^{1}H 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, ^{4}J 2.4 Hz, *m*C_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 (TiO*C*); 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, β = 102.517(2)°, V = 2855.8(3) Å^3, D_c = 1.262 g cm^{-3}, Z = 4. Of the 5004 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 60.94°$) with Mo-K$_\alpha$ (λ = 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, β = 97.875(3)°, V = 4360.7(5) Å^3, D_c = 1.228 g cm^{-3}, Z = 4. Of the 4399 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 52.73°$) with Mo-K$_\alpha$ (λ = 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 $P\bar{1}$ (no. 2), a = 9.6679(5), b = 12.1261(6), c = 13.9575(4) Å, α = 86.118(3), β = 72.704(3), γ = 67.257(2)°, V = 1438.8(2) Å^3, D_c = 1.458 g cm^{-3}, Z = 2. Of the 5428 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 52.75°$) with Mo-K$_\alpha$ (λ = 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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