DALTON COMMUNICATION

Organo-scandium and -yttrium complexes supported by a salicylaldiminato ligand

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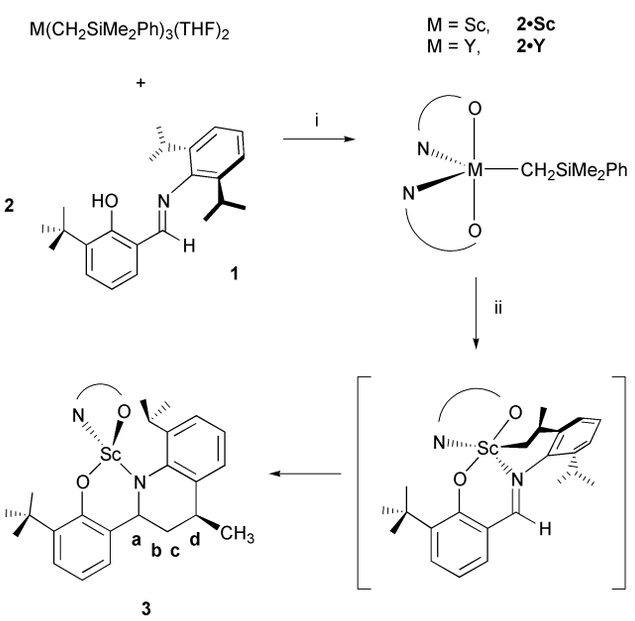
Reaction of a salicylaldiminato ligand with $M(CH_2SiMe_2Ph)_3(THF)_2$ (M = Sc, Y) leads to diastereoselective formation of highly thermally stable L_2MR complexes whose reactivity with dihydrogen to form Group 3 metal hydrides is described.

New ligand environments for supporting base free organo Group 3 complexes are of interest due to the potential of such complexes as olefin polymerization catalysts that do not require a co-catalyst. Examples include the β-diketiminato ligand,[1] amidinate[2] and bis-amidinate[3] donors, guanidinate anions,[4] linked amido/1,4,7-triazacyclononane[5] and amino/amidinate[6] chelates, Schrock's NON tridentate donor,[7] N,O[8,9] and N,P[10] macrocycles and bulky tetradentate salen ligands.[11] Related to the last example is the bidentate N,O salicylaldiminato ligand, which has been exploited in late transition metal catalysts to provide an effective ligand environment for olefin polymerization catalysts based on Ni(II)[12] and in the zirconium based Mitsui catalysts.[13] Herein we report new organometallic complexes of Sc and Y supported by this ligand framework.[14]

The bulky salicylaldiminato ligand **1** was prepared according to the literature procedure.[12] Salt metathesis routes employing Li or Na salts of the ligand and $MCl_3(THF)_3$ (M = Sc, Y) precursors were ineffective for clean ligand institution onto the Group 3 metal. However, the ligand can be smoothly attached *via* alkane elimination[15] as shown in Scheme 1, providing the base free organoscandium and organoyttrium derivatives **2·Sc** and **2·Y** directly. While the long known derivatives $M(CH_2SiMe_3)_3(THF)_2$[16] are somewhat thermally sensitive and best used *in situ*, we have found that the related compounds $M(CH_2SiMe_2Ph)_3(THF)_2$ are both more amenable to isolation in good to excellent yield, and serve as more convenient starting materials for alkane elimination protocols.



Scheme 1 Reagents and conditions: i, hexanes, 0 °C⟶RT, 24 hours; ii, 130 °C, 3 days, M = Sc, R = Me.

Compounds **2** are produced exclusively as one diastereomer, as indicated by ^{1}H NMR spectroscopy,[17] and neither exhibits any fluxional behaviour in solution on the NMR timescale. An X-ray crystallographic analysis of **2·Y**[18] (Fig. 1 gives an ORTEP[19] diagram along with selected metrical data) reveals that the isomer produced has pseudo C_2 symmetry with the oxygen donor atoms occupying the apical sites of a distorted trigonal bipyramid (O(1)–Y–O(2) = 159.93(5)°). In addition to the preference for more electronegative donors to occupy the axial sites, this arrangement in **2·M** is favored on steric grounds, allowing the bulky aryl groups on nitrogen to orient themselves away from each other above and below the N_2YC plane. Molecular mechanics calculations (MacSpartan Plus, Wavefunction Inc., Irvine, CA, 1996) show that other isomers

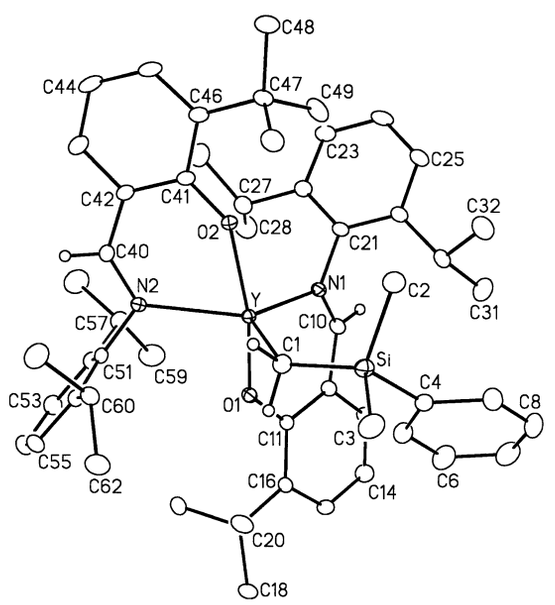


Fig. 1 Molecular structure of **2·Y** (hydrogen atoms omitted for clarity, apart from those attached to C(1), C(10) and C(40); thermal ellipsoids drawn to 30% probability level). Selected bond distances (Å) and angles (°): Y–O(1) 2.1473(13), Y–O(2) 2.1342(13), Y–N(1) 2.4238(16), Y–N(2) 2.4420(15), Y–C(1) 2.384(2); O(1)–Y–O(2) 159.93(5), O(1)–Y–N(1) 77.30(5), O(1)–Y–N(2) 90.62(5), O(1)–Y–C(1) 100.05(6), O(2)–Y–N(1) 97.03(5), O(2)–Y–N(2) 75.83(5), O(2)–Y–C(1) 99.23(7), N(1)–Y–N(2) 121.58(5), M(1)–Y–C(1) 122.07(6), N(2)–Y–C(1) 116.28(6), Y–C(1)–Si 131.36(11).

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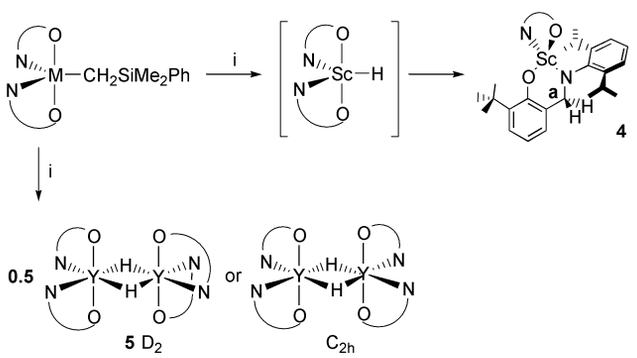
are characterized by rather severe steric interactions. A similar ligand arrangement is observed in the six coordinate zirconium bis-ligand complexes.[13]

Alkyl complexes **2** are highly thermally stable and exist in solution unchanged for several days at temperatures up to 60 °C. When heated at higher temperatures (130°, 3 days), conversion to a new species is observed; this process is clean for M = Sc, but not for M = Y where further chemistry ensues. The ^{1}H NMR spectrum of the product of thermolysis of **2·Sc** is consistent with a process involving metallation of the remaining alkyl group with a C–H bond of an isopropyl group, followed by a 1,3 migration of the Sc–C moiety to the aldimine carbon, producing the four coordinate species **3** (Scheme 1).[20] Connectivities were unequivocally established using 2D COSY and HMQC NMR experiments and within the detection limits of ^{1}H NMR spectroscopy, the reaction is >97% diastereoselective.

Complexes **2** react smoothly and cleanly with H_2 (4 atm, RT) to eliminate H_3CSiMe_2Ph and give metal hydrides. In the case of scandium, this species is not observed directly, but rather rearranges to give the product **4** (Scheme 2)[21] *via* a process



Scheme 2 Reagents and conditions: i, H_2, 4 atm, toluene, RT, 4 hours.

related to that described above for **3**. The molecularity of this reaction is unknown but likely an intramolecular 1,3 shift is involved. For the yttrium derivative, dimerization of the hydrido complex that results from hydrogenolysis of the alkyl group is favored over a similar 1,3 transfer of hydride to the aldiminato carbon. The dimeric nature of the complex **5**[22] is indicated clearly by the triplet observed for the bridging hydrides at 7.54 ppm ($J_{Y,H}$ = 32 Hz). Dimer **5** is produced with high diastereoselectivity and, although the NMR data are not able to distinguish between the D_2 symmetric *rac* diastereomer and the C_{2h} symmetric *meso* isomer, the *rac* isomer is most likely to be favored on steric grounds.

In conclusion, we have prepared new thermally stable, base free organoscandium and organoyttrium complexes incorporating the salicylaldiminato ligand **1** *via* a convenient and high yielding alkane elimination protocol. Hydrogenolysis forms reactive metal hydrides, whose olefin chemistry is currently being investigated. These compounds are neutral analogs of the Mitsui catalyst system based on Group 4 metals, and their role as olefin polymerization catalysts[13] and lactide polymerization initiators[23] is being explored.

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17 Selected NMR data for **2·M**: M = Sc: ^{1}H NMR (400 MHz, C_6D_6): 1.17, 0.49 (d, 1H, $^2J_{H,H}$ = 10 Hz, ScCH_2). ^{13}C NMR (100.6 MHz, C_6D_6): 40.97 (br, ScCH_2); 3.81, 2.76 (SiMe_2Ph). Anal. Calcd. for $C_{55}H_{73}N_2O_2SiSc\cdot0.5(C_6H_{14})$: C, 76.5; H, 8.9; N, 3.1. Found: C, 76.3; H, 8.5; N, 3.0%. M = Y: ^{1}H NMR (400 MHz, C_6D_6): 0.50, 0.43 (s, 2 × 3H, CH_2SiMe_2Ph); 0.39, 0.06 (dd, 1H, $^2J_{H,H}$ = 11, $^2J_{H,Y}$ = 3.5 Hz, CH_2SiMe$_2$Ph). ^{13}C NMR (100.6 MHz, C_6D_6): 32.42 (d, $^1J_{C,Y}$ = 49 Hz, YCH_2). Anal. Calcd. for $C_{55}H_{73}N_2O_2SiY$: C, 72.5; H, 8.1; N, 3.1. Found: C, 72.1; H, 8.3; N, 3.1%.
18 Crystallographic data for **2·Y**: single crystals were grown from hot hexanes and suspended in inert oil prior to mounting on the diffractometer. $C_{55}H_{73}N_2O_2SiY$, M = 911.15, monoclinic, space group $P2_1/c$, a = 24.4752(14), b = 10.0224(5), c = 23.2570(13) Å, β = 115.7071(10)°, V = 5140.3(5) Å^3, T = −80 °C, Z = 4, D_{calc} = 1.177 g cm^{-1}, μ = 1.198 mm^{-1}, Bruker P4/RA/SMART 1000 CCD diffractometer, λ(Mo-Kα) = 0.71073 Å, 10466 unique reflections, final residuals R_1 [$F_o^2 \geq 2\sigma(F_o^2)$] = 0.0356, wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$] = 0.0906 for 8301 reflections and 550 parameters. CCDC reference number 175512. See http://www.rsc.org/suppdata/dt/b1/b108336h/ for crystallographic data in CIF or other electronic format.
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20 Selected NMR data for **3**: ^{1}H NMR (400 MHz, C_6D_6): 4.50 (dd, 1H, $^3J_{H,H}$ = 4.0, 1.5 Hz, H_a); 3.34 (m, 1H, H_d); 2.15 (ddd, 1H, J = 14, 6, 1.5 Hz, H_b); 1.29 (d, 3H, J = 5 Hz, CH_dCH_3); 0.80 (m, 1H, H_c). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): 174.70 (*C*HNAr); 53.39 (CH_a); 32.83 ($CH_{b,c}$); 27.42 (CH_d Me); 22.91 (CH_dCH_3). Anal. Calcd. for $C_{46}H_{59}N_2O_2Sc$: C, 77.1; H, 8.3; N, 3.9. Found: C, 76.6; H, 8.7; N, 3.8%.
21 Selected NMR data for **4**: ^{1}H NMR (400 MHz, C_6D_6): 7.81 (s, 1H, C*H*NAr), 4.71 (d, 1H, $^2J_{H,H}$ = 15 Hz, CH_2, $^1J_{C,H}$ = 100(4) Hz), 4.46 (d, 1H, CH_2, $^1J_{C,H}$ = 110(4) Hz). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): 176.16 (*C*HNAr), 60.14 (CH_a).
22 Selected NMR data for **5**: ^{1}H-NMR (400 MHz, C_6D_6): 8.14 {s, 4H, C*H*(NAr)}, 7.54 (t, 2H, $^1J_{H,Y}$ = 32 Hz, μ-*H*). Anal. Calcd. for $[C_{46}H_{61}N_2O_2Y]_2$: C, 73.0; H, 8.5; N, 3.5. Found: C, 73.3; H, 8.2; N, 3.6%.
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